This Document Contains
Missing Page/s That Are
Unavailable In The
Original Document
112, 113

Best Available Copy

AD 287788

Contractor: Army Chemical Center

Contract No.: DA 18-108-405-CML-518
DA 18-108-CML-7008

October 30, 1962

ASTIA

NOV 9 1962

TISIA

Final Report

Title: THE ACCELERATED
CORROSION OF METALS
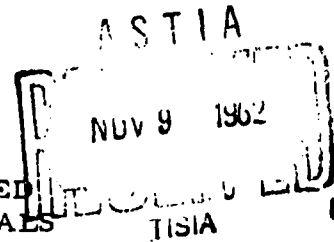
Henry Leidheiser, Jr.

Part A. "A Survey of the Effect of 40 Liquid Metals and Alloys on the Oxidation and Loss of Coherence of 13 Metals at Room Temperature" by David A. Jackson, Jr., and Henry Leidheiser, Jr.

Part B. "Catalytic Acceleration of the Corrosion of Aluminum, Iron, and Copper in Aqueous Solution at Room Temperature" by David A. Jackson, Jr., and Henry Leidheiser, Jr.

Part C. "The Rapid Corrosion of Metals at Room Temperature in the Presence of Hydrogen Sulfide, Various Salts, and Water Vapor" by W. Roger Buck, III, and Henry Leidheiser, Jr.

Part D. "The Very Rapid Oxidation of Aluminum at Room Temperature When in Contact with Mercuric Iodide" by David A. Jackson, Jr., and Henry Leidheiser, Jr.

Part E. "An Ultrastructure Study of the Corrosion Product Formed during the Catastrophic Corrosion of Aluminum in the Presence of Mercury and an Hypothesis for Explaining the Structure Observed" by Anton N. J. Heyn

Covering the Period: September 15, 1959 - September 15 1962

Copy _____ of _____ Copies

TABLE OF CONTENTS

PART A

"A Survey of the Effect of 40 Liquid Metals and Alloys on the
Oxidation and Loss of Coherence of 13 Metals at
Room Temperature"

By

David A. Jackson, Jr., and Henry Leidheiser. Jr.

ABSTRACT

Two outstanding examples of the deterioration of metals in contact with liquid metals and alloys at room temperature were observed in this study: (1) the rapid oxidation of aluminum and magnesium in the presence of mercury and its alloys, and (2) the cracking and loss of internal cohesion of such metals as aluminum, zinc, silver, cadmium, lead, and tin in the presence of gallium and its alloys. The most effective liquid metal alloy in the attack on aluminum was the 80% Hg-20% Tl alloy. The most effective liquid metal alloy in the attack on magnesium was the 95% Hg-5% In alloy.

INTRODUCTION

The extremely deleterious effect of mercury on aluminum has been documented in many scientific reports and publications and is well known in the chemical industry. Although the phenomenon is well known, there are very few studies which are helpful in understanding the factors controlling the rate of deterioration. This portion of the overall study was made in the very early phases when prime consideration was being given to picking a system for quantitative study. These preliminary survey-type experiments culminated in the decision to study the oxidation of pure aluminum in contact with mercuric iodide, which study is summarized in Part D of this report. The results of the study with the liquid metals are summarized here because some of the observations may be useful to other workers concerned with the very rapid deterioration of metals. It must be emphasized that these experiments are preliminary in nature and that they were only carried out for the purpose of choosing a system for quantitative study.

EXPERIMENTAL PROCEDURE

All experiments were carried out at room temperature (25-35°). In a transparent, plastic reaction chamber. The chamber was maintained at a relative humidity of 79-82%, as determined by a wet bulb and dry bulb humidity gauge, through the use of a saturated solution of $BaCl_2$ and a fan. The chamber was appropriately baffled so that the reaction product was not disturbed by the moving air.

A Polaroid Land camera equipped with a #3 close-up lens attachment was used to take pictures of many of the experiments. These photographs served to make comparisons between experiments carried out at different times.

METALS USED

The following metals were used as corrosion samples or in the preparation of the various mercury or gallium alloys.

Aluminum. Pigs of 99.999% aluminum were obtained from the Reynold Metals Company. The analysis for this casting was as follows:

Si	Cu	Mg
0.0003	0.0001	0.0010

The lot number for the casting was 4R133.

Magnesium. Rods, 15/16" in diameter of magnesium, and designated as 99.95% pure, were obtained from A. D. Mackay, Inc. No analysis was listed.

Tin. Bars of purified tin were obtained from the Fisher Scientific Company, but no analysis was available.

Copper. Rods, 3/8" in diameter, were obtained from the American Smelting and Refining Company. The purity was listed as 99.999%.

Zinc. Sticks of 1/4" diameter zinc rods were obtained from the Fisher Scientific Company. They were described as C.P. grade and had the following impurities:

As	Fe	Pb
0.000000%	0.002	0.003

The lot number for the casting was 793800.

Titanium. Rods, 5/8" in diameter, of commercial grade A-70 titanium were obtained from the Crucible Steel Company of America , and had the following percentage analysis:

C	H	N	Fe
0.04	0.0029	0.02	0.20

Lead. Sticks, 1/4" in diameter, were obtained from the Fisher Scientific Company and had the following percentage analysis:

As	Bi	Cu	Fe	Ni	Ag
0.00000	0.00001	0.0003	0.001	0.0001	0.0001

Zirconium (Zircaloy-2). A three-foot rod of Zircaloy-2 was obtained from the Hanford Laboratories. The following analysis accompanied the rods:

Sn	Fe	Cr	Ni	N	Al	H
1.5%	0.12%	0.10%	0.05%	70 ppm.	60 ppm.	50 ppm.

Cadmium. A small ingot of 99.999% pure cadmium was obtained from the Consolidated Smelting and Refining Company of Canada.

Antimony. Chips of high purity antimony were obtained from the Bradley Mining Company. No analysis is available.

Silver. A small rod of 3/8" diameter silver was obtained from the Consolidated Smelting and Refining Company of Canada. It was listed as 99.999% pure.

Bismuth. A small ingot of intermediate grade 99.999% pure bismuth was obtained from the Consolidated Smelting and Refining Company of Canada.

Nickel. Shavings from rods of 99.92% Ni were used. They were obtained from Crucible Steel Company of America.

Barium. A small rod of 99.5% pure barium was obtained from A. D. Mackay Company.

Manganese. Manganese in the form of small platelets was obtained from United Mineral and Chemical Corp. The purity listed was 99.99+%.

Arsenic. Arsenic metal in chunk form was obtained from the United Mineral and Chemical Corp. The purity was listed as 99.99%.

Platinum
Palladium
Gold   Shavings of metals of unknown impurity
Ruthenium   composition were used.
Rhodium
Iridium

Indium. Metal, 99.7% pure, was obtained in ingot form from the Consolidated Smelting and Refining Company of Canada

Thallium. A small rod, 1/2" in diameter, of 99.99% pure thallium was obtained from A. D. Mackay, Inc.

Gallium. Gallium metal 99.99% pure was obtained from Fisher Scientific Company and had 0.0051% Pb listed as the only significant impurity.

Mercury. Triply distilled, purified reagent grade mercury was obtained from the Fisher Scientific Company. The analysis indicated that gold and silver did not exceed 0.005%.

Iron. Common, cold-rolled steel was obtained from a local distributor.

PREPARATION OF SAMPLES

The majority of the metal samples were machined in the form of discs, 1/2" in diameter and 1/4" thick, with a small recess on one face to serve as a pool for the liquid metal. Only the 3/8", 99.999% pure copper rods and the 15/16" 99.95% pure magnesium rods were used in the diameter received. Some of the other low-melting metals were recast to the desired size before machining. After machining, the samples were degreased in ether and dried before being transferred to the reaction chamber. After humidity equilibrium was achieved in the chamber, a drop or two of etching solution was placed on the sample, followed by the liquid metal or salt used as the corrosion promoter.

TYPE OF ETCHANT

For all samples except titanium and zirconium, the etching solution was HCl (gas) dissolved in 95% ethyl alcohol to the extent where a 2M to 3M solution was achieved. For the titanium and zirconium samples, several fluoride etchants were used:

a) Solid HgF_2 + 2M HF

b) 1M HF

c) Solid NaF + 2M H_2SO_4

EXPERIMENTAL RESULTS

ALUMINUM

The results obtained with many different liquid alloys are summarized in Table I. The general type of oxidation observed with the mercury alloys was similar to that obtained with pure mercury and many mercury salts in which long filaments of oxide grew from the metal surface. Figure 1 is typical of the appearance of the majority of the samples exposed to the alloys in column 1 of Table I

In the case of the gallium alloys, the samples did not generally exhibit as large an amount of oxidation as observed with the mercury alloys, but rather the samples deteriorated by cracking. Wetting of the surfaces of the sa. ples by the gallium alloys took place only in the recessed area directly under the pool of liquid metal. However, once wetting began, the liquid metal penetrated the sample largely along grain boundaries. In some cases, the location of the cracks did not appear to be related to the location of the gra .. boundaries. Figure 2 shows several typical experiments with six gallium alloys.

Figure 1.   Typical type of oxidation observed when pure aluminum was exposed to the mercury alloys listed in column 1 of Table I. This particular experiment was carried out with $HgBr_2$, $HgCl_2$, and HgI_2, but it is typical of the results obtained with liquid mercury alloys.

Figure 2.   The attack on aluminum by gallium alloys. The following
             alloys were used: #1, pure Ga; #3, 95% Hg-5% Ga; #5,
             90% Hg-10% Ga; #8, 75% Hg-25% Ga; #9, 80% Ga-20% In;
             #11, 65% Ga-35% In. No white oxide was apparent in samples
             containing no mercury. Cracking and splitting took place on
             all samples. The sample attacked by pure Ga (#1) cracked
             severely but did not spontaneously separate. The white oxide
             was scraped away from samples #3, #5, and #8 to show the
             fragments. Reaction time - 76 hours.

TABLE I

A Tabulation of the Experimental Results Obtained when Cylinders of 99.999% Aluminum Were Exposed to Various Liquid Metals and Alloys

Alloys Which Caused Severe Oxidation of Aluminum	Alloys Which Caused Cracking of Aluminum	Alloys Showing No Severe Deleterious Effect on Aluminum
Hg	Ga	All alloys caused either appreciable oxidation or
95% Hg - 5% Ga	95% Hg - 5% Ga	led to cracking.
90% Hg - 10% Ga	90% Hg - 10% Ga	
75% Hg - 25% Ga	75% Hg - 25% Ga	
95% Hg - 5% In	80% Ga - 20% In	
95% Hg - 5% Tl	65% Ga - 35% In	
80% Hg - 20% Tl	95% Ga - 5% Zn	
98% Hg - 2% Sn	92% Ga - 8% Sn	
98% Hg - 2% Bi	Ga satd. with Tl	
82% Ga - 18% In	Ga satd. with Cu	
70% Ga-18% In-12% Sn	70% Ga-18% In-12% Sn	
Hg satd. with Pt	Ga satd. with Ag	
Hg satd. with Pd	90% Ga - 10% Cd	
Hg satd. with Au	Ga satd. with Ni	
Hg satd. with Ag	82% Ga-12% Sn-6% Zn	
Hg satd. with Ba	70% Ga-18% In-12% Sn	
Hg satd. with Mn	98% Hg-2% Ga alloy satd. with In	
Hg satd. with Mg		
Hg satd. with Cu	95% Hg - 5% Ga alloy satd. with In	

TABLE I (cont.)

Alloys Which Caused Severe Oxidation of Aluminum	Alloys Which Caused Cracking of Aluminum	Alloys Showing No Severe Deleterious Effect on Aluminum
98% Hg – 2% Pb	95% Hg – 5% Tl alloy satd. with In	
98% Hg – 2% Zn		
95% Hg – 5% Cd		
Hg satd. with Ru		
Hg satd. with Ir		
Hg satd. with Rh		
51% Hg–41% In–8% Tl		
73% Hg–17% In–10% Tl		
98% Hg – 2% Ga alloy satd. with Tl		
95% Hg – 5% Ga alloy satd. with Tl		
98% Hg – 2% Ga satd. with In		
95% Hg – 5% Ga satd. with In		

COPPER

The following liquid metals and alloys were studied:

Pure Hg	Hg satd. with Pt	Pure Ga
95% Hg - 5% In	Hg satd. with Pd	80% Ga - 20% In
90% Hg - 10% In	Hg satd. with Au	92% Ga - 8% Sn
80% Hg - 20% In	Hg satd. with Ag	95% Ga - 5% Zn
98% Hg - 2% Pb	Hg satd. with Ba	82% Ga - 18% In
98% Hg - 2% Zn	Hg satd. with Mn	Ga satd. with Pb
98% Hg - 2% Sn	Hg satd. with Ir	Ga satd. with Tl
95% Hg - 5% Tl	Hg satd. with As	82% Ga-12% Sn-6% Zn
90% Hg - 10% Tl	Hg satd. with Rh	70% Ga-18% In-12% Sn
80% Hg - 20% Tl	Hg satd. with Mg	73% Hg-17% In-10% Tl
70% Hg - 30% Tl	Hg satd. with Ru	
95% Hg - 5% Cd	51% Hg-41% In-8% Tl	
95% Hg - 5% Ga	95% Hg-5% Ga satd.	
90% Hg - 10% Ga	with Tl	
98% Hg - 2% Bi	95% Hg-5% Ga satd.	
Hg satd. with Cu	with In	

All the copper samples were readily wet by the liquid alloys but no evidence of oxidation, cracking, or peeling was observed in 90 hours. The samples could not be broken even when a strong bending force was applied.

LEAD

None of the alloys studied exhibited a tendency to promote the oxidation of lead to any visible extent. However, many of the alloys did cause a loss of coherence of the lead as shown by the fact that bending the samples resulted in fragmentation. Those alloys which did and did not cause a loss of coherence are listed in Table II.

Because of the survey-nature of these experiments, it is not possible to draw clear-cut conclusions. It did appear, however, that a necessary preliminary to the loss of coherence was wetting of the lead surface by the

liquid metal. Since wetting can be affected by thin surface films, it must be

recognized that some of the alloys which did not cause a loss of coherence

may have done so under different conditions of surface preparation.

TABLE II

A Tabulation of the Liquid Metals and Alloys which Did and Did Not
Cause a Loss of Coherence of Lead Samples

Those Alloys Which Caused a Loss of Coherence	Those Alloys in Which No Loss of Coherence was Observed
95% Hg - 5% In	Pure Ga
90% Hg - 10% In	Ga satd. with Pb
80% Hg - 20% In	95% Ga - 5% Zn
98% Hg - 2% Zn	82% Ga - 18% In
98% Hg - 2% Sn	Ga satd. with Tl
95% Hg - 5% Cd	92% Ga - 8% Sn
95% Hg - 5% Ga	82% Ga-12% Sn-6% Zn
90% Hg - 10% Ga	98% Hg - 2% Bi
80% Ga - 20% In	Hg satd. with Cu
70% Ga-18% In-12% Sn	95% Hg - 5% Tl
Hg satd. with Pt	90% Hg - 10% Tl
Hg satd. with Pd	80% Hg - 20% Tl
Hg satd. with Ir	70% Hg - 30% Tl
Hg satd. with As	80% Hg-18% Tl-2% Pb
Hg satd. with Rh	98% Hg - 2% Pb
Hg satd. with Mg	Hg satd. with Au
Hg satd. with Ru	Hg satd. with Ag
	Hg satd. with Ba
	Hg satd. with Mn

MAGNESIUM

The typical result obtained when magnesium was contacted with

mercury or its alloys at high relative humidities is shown in Figure 3. The

oxide generally formed in a column which had a layered structure. The

oxide was voluminous and X-ray diffraction analysis did not yield rings

characteristic of a crystalline compound. The liquid metal alloys which did
and did not promote the rapid oxidation of magnesium are listed in Table II.
In no case did observable cracking or loss of coherence occur.

Figure 3.   The typical appearance of magnesium samples after exposure
to liquid mercury alloys at high relative humidity for 24 hours.

TABLE III

A Tabulation of the Liquid Metals and Alloys
Which Did and Did Not Cause Appreciable Oxidation
of Magnesium Samples

Those Alloys Which Caused Rapid Oxidation of Magnesium	Those Alloys Which Did Not Cause Rapid Oxidation of Magnesium
Hg	Ga
95% Hg - 5% In	80% Ga - 20% In
÷ 90% Hg - 10 % In	82% Ga-12% Sn-6% Zn
÷ 80% Hg - 20% In	70% Ga-18% In-12% Sn
98% Hg - 2% Pb	92% Ga - 8% Sn
98% Hg - 2% Zn	73% Hg-17% In-10% Tl
95% Hg - 5% Tl	51% Hg-41% In-8% Tl
90% Hg - 10% Tl	# Ga satd. with Ag
80% Hg - 20% Tl	# 95% Ga - 5% Zn
70% Hg - 30% Tl	# 92% Ga - 8% Sr
80% Hg-18% Tl-2% Pb	# Ga satd. with Tl
98% Hg - 2% Sn	
95% Hg - 5% Cd	
95% Hg - 5% Ga	
90% Hg - 10% Ga	
98% Hg - 2% Bi	
Hg satd. with Cu	
# Hg satd. with Ir	
# Hg satd. with Rh	
# Hg satd. with Ru	
# Hg satd. with Pt	
# Hg satd. with Pd	
# Hg satd. with Au	
# Hg satd. with Ag	
# Hg satd. with Ba	
# Hg satd. with Mn	
# 98% Hg - 2% Ga alloy satd. with Tl	
# 95% Hg - 5% Ga alloy satd. with Tl	
# 98% Hg - 2% Ga alloy satd. with In	
# 95% Hg - 5% Ga alloy satd. with In	
*# Ga	

TABLE III (cont.)

Those Alloys Which Caused Rapid Oxidation of Magnesium	Those Alloys Which Did Not Cause Rapid Oxidation of Magnesium
÷# Ga satd. with Cu	
÷# Ga satd. with Ni	
÷# 90% Ga - 10% Cd	

÷ -   In these experiments the total amount of oxidation was much less than with pure mercury.

-   These experiments were carried out with 99.95% pure Mg. All the other experiments were carried out with 99.99% pure Mg.

STAINLESS STEEL

Samples of 304 stainless steel were exposed to the 20 different

liquid metals and alloys listed below. No deleterious effects were ob-

served. There was no obvious oxidation, cracking, or loss of coherence.

Hg	98% Hg - 2% Zn
95% Hg - 5% Tl	98% Hg - 2% Sn
80% Hg - 20% Tl	Ga
70% Hg - 30% Ti	95% Hg - 5% Ga
95% Hg - 5% In	90% Hg - 10% Ga
90% Hg - 10% In	75% Hg - 25% Ga
80% Hg - 20% In	80% Ga - 20% In
70% Hg - 30% In	65% Ga - 35% In
95% Hg - 5% Cd	95% Ga - 5% Sn
80% Hg-18% Tl-2% Pb	95% Ga - 5% Zn

TIN

A number of the liquid metal alloys with gallium as the major con-

stituent had the effect of reducing coherence in the tin samples. Many of

the samples broke readily along grain boundaries when a weak bending force
was applied with a pair of pliers. In no case was rapid oxidation of the
samples observed. The alloys studied and their effect on coherence are
given in Table IV.

TABLE IV

A Tabulation of the Liquid Metals and Alloys Which Did
and Did Not Cause a Loss of Coherence

Those Alloys Which Caused a Loss of Coherence	Those Alloys in Which No Loss of Coherence · as Observed
Ga	Hg
90% Hg - 10% Ga	95% Hg - 5% In
80% Ga - 20% In	90% Hg - 10% In
82% Ga-12% Sn-6% Zn	80% Hg - 20% In
70% Ga-18% In-12% Sn	98% Hg - 2% Pb
	98% Hg - 2% Zn
	98% Hg - 2% Sn
	80% Hg-18% Tl-2% Pb
	95% Hg - 5% Tl
	90% Hg - 10% Tl
	80% Hg - 20% Tl
	70% Hg - 30% Tl
	95% Hg - 5% Ga
	98% Hg - 2% Bi
	Hg satd. with Cu
	Hg satd. with Pt
	Hg satd. with Pd
	Hg satd. with Au
	Hg satd. with Ag
	Hg satd. with Ba
	Hg satd. with Mn
	Hg satd. with Ir
	Hg satd. with As
	Hg satd. with Rh
	Hg satd. with Mg
	Hg satd. with Ru
	Ga satd. with Pb
	Ga satd. with Tl

TABLE IV (cont.)

Those Alloys Which Caused a Loss of Coherence	Those Alloys in Which No Loss of Coherence was Obs...ved
	95% Ga - 5% Zn
	95% Hg - 5% Ga
	satd. with Tl
	95% Hg - 5% Ga
	satd. with In
	92% Ga - 8% Sn
	51% Hg-41% In-8% Tl
	73% Hg-17% In-10% Tl

TITANIUM

Titanium samples were exposed to all of the liquid metals and alloys used in this investigation. In no case was there any evidence of oxidation, cracking, or loss of coherence. Along with the EtOH-HCl etchant used with other metals, studies were also carried out in which the EtOH-HF and 2M HCl-0.2M NaF etchants were used. The use of fluorides, known to increase the activity of titanium, were without effect in increasing the rate of oxidation or in promoting a loss of coherence.

ZINC

A serious loss in coherence, with rupture primarily along grain boundaries, was observed with all the liquid metals and alloys. The loss of coherence appeared to be greater in the case of those alloys in which gallium was the major constituent than in those alloys in which mercury was the major constituent. No apparent increase in oxidation was observed.

ZIRCONIUM

None of the liquid metals or alloys were effective in causing rapid oxidation of zirconium or resulted in any obvious loss in coherence. Experiments were carried out with both the standar EtOH-HCl etchant and 1M HF with similar results.

MISCELLANEOUS EXPERIMENTS WITH ANTIMONY, CADMIUM, AND SILVER

Small cylinders of cadmium and silver were severely cold worked by means of hammering and a cylinder of antimony was prepared by machining. A drop of pure gallium was placed on each cylinder and it remained in contact with the metal for 70 hours. Solidification of the liquid alloy took place on the antimony and silver samples. The cadmium sample was weakened by this exposure because it readily cracked when a small bending force was applied.

A similar experiment was carried out with the 70% Hg-30% Ga alloy. Under these conditions all three metals suffered a loss of coherence and cracked or broke when a small bending force was applied.

IRON

In order to investigate the possibility of cracking of hydrogen-charged steel by gallium and its alloys, the following tests were made. Common, cold-rolled steel was machined into flat discs approximately 1.8 cm. in diameter, 1 mm. thick and having approximately 5 cm.^{2} total surface area. Each sample was charged with hydrogen by making it the cathode in a 1 N

H_2SO_4 solution, with a current density of 40 mamp./cm.^{2} for fifteen min-
utes. The anode was a coiled platinum wire. After charging, the samples
were rinsed in distilled water, dried, and treated with a gallium alloy and
the EtOH-HCl etching agent. The experiment was carried out at room
temperature (25-30°C) in the atmosphere (75-95% relative humidity). The
liquid alloys were allowed to remain in contact with the steel discs for three
days. The samples were then examined for any cracking, pitting or oxi-
dation. The liquid metal alloys were easily removed from the samples
leaving the surface clear of any apparent rust. Close examination of the
samples at 200-300 X showed minute pits. No cracking or severe damage
was observed. A very slight discoloration was observed on the steel direct-
ly under where the liquid metal had been placed. No wide-spread alloying
or penetration could be detected. After visual inspection, the samples were
flexed several times by bending with pliers. In no case did the samples
break any easier than the untreated samples, and it is assumed that no
significant weakening of the steel was caused by the liquid metals.

Alloys and metals used in this experiment were as follows:

Ga
92% Ga - 8% Sn
82% Ga - 18% In
70% Hg - 30% Ga

LOW TEMPERATURE STUDIES

In order to investigate the cracking of aluminum and magnesium samples by mercury near the freezing point of mercury, a special reaction vessel was constructed. The vessel consisted of two pyrex tubes, approximately 9/16" inside diameter, 6" long, each sealed flat on one end, and connected together with a 19/38 standard-taper joint. The vessel was mounted in a vertical position, with the lower half immersed in the cooling bath. The upper half had a short side arm tube projecting at a 45° angle. The end of the side arm tube was covered with a rubber diaphragm containing a small pin hole. This diaphragm served as an air-tight opening through which a finely-drawn eye dropper was inserted when admitting the etching solution and liquid metal alloy. At the extreme upper end of the vessel a drying agent (Drierite) was packed and held in place by cotton wadding.

The metal samples were machined in the shape of 1/2" diameter cylinders, 3/4" long. A hole was drilled in the end of each cylinder to accommodate a thermometer bulb. Before each test was run, the vessel was filled with argon gas and sealed to keep oxidation at a minimum.

The cooling liquid was chosen according to its freezing point. Since the freezing point of mercury is -38.87 C., it was desired to have a cooling bath which would maintain a temperature in this region. Ethylenedichloride (M.P. = 35.3°C.) was first chosen, but later it was found that pyridine (M.P. = 41.5°C.) was more satisfactory. The pyridine was frozen with dry ice and acetone, broken up, and transferred into a Dewar flask as a slush.

The reaction vessel was lowered into the cooling bath, and the temperature of the sample soon achieved a constant value of approximately -38°.

In general, the samples were unstressed except by the amount induced by machining. Several samples, however, were pre-stressed with a hydraulic press. These samples appeared to be attacked the greatest amount.

The attack by pure mercury on stressed aluminum indicated deep penetration, especially at grain boundaries. Some cracking took place at grain boundaries, but to a much lesser degree than in the attack by pure gallium at room temperature. The attack by pure mercury on magnesium was indeterminate; very little surface alloying took place, but this was probably due to the short period of time that the reaction was allowed to proceed. (The cooling bath held the temperature at -38°C. for about 6 or 7 hours only.) The only apparent reaction was the small amount of oxidation by air leakage. In general, the amalgamation processes were much slower than at room temperature. Even the initial oxidation process was slower when the cold samples were exposed to air. Mercury alloys seemed to be no more effective in cracking Al or Mg than the pure metals.

DISCUSSION

In this survey of the accelerated corrosion of various metals by liquid metals and metallic salts, two outstanding examples have been noted: 1) the rapid oxidation of aluminum and magnesium in the presence of mercury and its alloys, and 2) the cracking and loss of internal cohesion of such metals as aluminum, zinc, silver, cadmium, lead and tin in the presence of gallium and its alloys. Metals having an exceptionally protective oxide film had very high resistance to attack by the liquid metals. Such were the cases with titanium, zircaloy-2, and stainless steel. The use of fluoride etching agents - materials which are known to destroy passivity in some metals - did not render these metals susceptible to attack by liquid alloys. Copper was wet by many of the liquid alloys but no apparent catastrophic deterioration of the metal occurred.

Mercury alloys of platinum, palladium, gold, silver, ruthenium, iridium, and rhodium were no more effective than pure mercury in the attack on aluminum or magnesium. The most effective liquid metal alloy in the attack on aluminum was the 80% Hg-20% Tl alloy; the most effective liquid metal alloy in the attack on magnesium was the 95% Hg-5% In alloy.

The cracking of aluminum by gallium and its alloys has been studied at room temperature. This temperature is near the freezing point of gallium. It is thought that penetration of the samples by gallium might be followed by a local solidification of an alloy in very small crevices. Possibly, this

freezing would lead to stresses great enough to promote cracking or loss of coherence. Experiments at low temperatures near the freezing point of mercury have given some indication that this may be so since the aluminum samples appeared to show a loss in coherence when exposed to mercury at temperatures first above the melting point.

Pre-stressed samples are known to be highly embrittled by liquid metal attack. For example, when pre-stressed silver was exposed to the 70% Hg-30% Ga alloy, the sample broke apart easily when a bending force was applied. Normally, silver is highly ductile.

PART B

"Catalytic Acceleration of the Corrosion of Aluminum,
Iron, and Copper in Aqueous Solution at Room Temperature"

By

David A. Jackson, Jr., and Henry Leidheiser, Jr.

ABSTRACT

The corrosion of iron in mineral and fruit acids at room temperature is greatly accelerated in the presence of Group VIII metals present originally in the solution in the ionic state. The average relative effectiveness decreased in the order: platinum, rhodium, palladium, iridium, ruthenium, osmium. cobalt, and nickel. The maximum corrosion rates in 1N and 2N solutions were 100-180 mg./cm.^{2}/hour. These rates appeared to be limited by diffusion of the reactants to or the products away from the surface. Very rapid corrosion of iron was obtained in 2N acids containing 10^{-4}M PtCl$_4$ and 0.5M NaI. Severe pitting and perforation of a 1/4" thick sample as well as dislodgement of fragments from the sample were observed. A series of experiments carried out as a function of pH indicated that iron begins to corrode at an appreciable rate below pH 5.

Very rapid corrosion of aluminum and a number of alloys at room temperature was obtained in mineral acids containing ions of the platinum metals, mercury, or combinations of two metals. Rates as high as 200 mg./cm.^{2}/hour were obtained in 2N HCl. Pure aluminum corroded at a rate in excess of 1 mg./cm.^{2}/hr. in water and 2N NaCl containing 10^{-3}M Hg(II) plus In(III).

The platinum metals were not effective in increasing the corrosion rate of copper in 2N HCl or H$_2$SO$_4$ at room temperature. Palladium, platinum, and rhodium, originally present as ions, were effective in inhibiting the corrosion of copper in 2M HNO$_3$ at room temperature.

INTRODUCTION

Previous studies indicated that the platinum metals are very effective in increasing the rate of corrosion of metals in various acids at the boiling point (1, 2). The motivation for the experiments summarized herein was to make a survey of the effect of the Group VIII metals on the corrosion of iron, aluminum, and copper in order to choose a system for quantitative study as well as to assist in asking significant questions. As the work progressed, it was decided to investigate also the effect of mercury and indium on the corrosion of aluminum and its alloys.

Quantitative and sophisticated experiments were not carried out as originally planned because the decision was made to place major emphasis on a quantitative study of the oxidation of aluminum in contact with mercuric iodide in an atmosphere of moist air. These experiments are summarized in Part D of this report.

EXPERIMENTAL

Metals Used

Iron. Rods, 0.5" in diameter, of Ferrovac E iron were obtained from the Crucible Steel Company and had the following percentage analysis:

C	Mn	P	S	Si	Ni
0.007	0.002	0.002	0.007	0.006	0.02

Cr	V·	W	Mo	Cu	Al
0.01	0.008	0.02	0.02	0.006	0.010

Co	N	O_2	H_2
0.006	0.00043	0.0057	0.000050

Aluminum. Five standard types of aluminum alloys and two high purity aluminum samples were obtained from the Reynolds Metals Company and had the following percentage analysis:

Alloy Designation	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Others Each	Total	Al
EC Hill	---	---	---	---	---	---	---	---	---	---	99.45 min.
2014	.8	---	4.5	.8	.4	---	---	---	---	---	remainder
360	9.5	---	---	---	.5	---	---	---	---	---	"
5456	.14	.26	.12	.78	5.35	.14	.07	.03	.05 max.	.15 max.	"
6101	.5	---	---	---	.6	---	---	---	---	---	"
7079-T6	---	---	.6	.2	3.3	.15	4.5	---	---	---	"
R-5-0's	.0003	---	.0001	---	.0. 0	---	---	---	---	---	99.9986 min.

Copper. Samples, 99.999% pure, was obtained from the American Smelting and Refining Company in the form of rods, 3/8" in diameter. Corrosion samples, 1/4" in length, were machined from the rods.

Procedure

The iron samples were machined in the form of flat cylinders approximately 0.50" diameter and 0.25" in length. Degreasing with ethyl ether was followed by slightly etching the samples in boiling dilute HCl or H_2SO_4, rinsing in distilled water, and drying under a heat lamp.

The aluminum alloys were received in the form of 0.25" flat sheets several inches long, cast pigs, or cast rods 0.625' diameter. Samples, 0.50" in diameter, were punched out with an hydraulic punch and die from the flat sheets. These punched samples were distorted so that further machining was necessary to obtain a uniform sample size of approximately 0.47" diameter and 0.25" in length. Samples cut from the cast pigs or cast rods were somewhat larger (0.50" in diameter and 0.25" in length).

Each sample was lightly etched, washed, and dried just prior to the individual experiment. The samples were placed in flasks containing the various salt-acid solutions, allowed to remain for the desired length of time without stirring at room temperature, and finally removed, rinsed in distilled water, dried, and weighed to determine the loss due to corrosion. Surface area measurements were made with the help of a micrometer, and the values for the corrosion rates as weight-loss per square centimeter were calculated. It should be noted that in many cases the aluminum samples

underwent a great decrease in size. The corrosion rates were calculated on
the basis of no change in surface area, however. Thus the calculated cor-
rosion rates were somewhat less than if the change in surface area had been
taken into account.

RESULTS WITH IRON

Corrosion in HCl. The results obtained in 1M HCl over a period of 24 hours in the presence of 10^{-4}M Group VIII chloride are summarized in Figure 1. Similar experiments in the presence of 10^{-3}M Group VIII chloride are summarized in Figure 2.

The results obtained in 2M HCl containing 10^{-3}M Group VIII chloride over a period of 60 minutes are summarized in Figures 3 and 4. Since the vertical scale is so different in the two figures, data for ruthenium are given in both figures in order to relate the two figures better.

It will be noted that platinum was the most effective in all instances in causing very rapid corrosion; rhodium, palladium, and ruthenium were intermediate in effectiveness; and iridium, osmium, nickel, and cobalt were ineffective. Additions of platinum to the acid caused the corrosion rate of iron to increase by almost three orders of magnitude.

Corrosion in H_2SO_4. The results obtained in 0.5M H_2SO_4 over a period of 24 hours are given in Figure 5 for 10^{-4}M added Group VIII chloride and in Figure 6 for 10^{-3}M Group VIII chloride. It will be noted that platinum was the most effective in increasing the rate in this medium also, and nickel and cobalt were relatively ineffective.

Mixtures of Group VIII Chlorides   It was next of interest to determine if mixtures of two of the Group VIII chlorides were any more effective than single additions of a Group VIII chloride. The first experiments were carried out with 10^{-3}M platinum chloride plus 10^{-3}M of a second Group VIII

Figure 1. The corrosion of iron in 1M HCl in the presence of 10^{-4}M Group VIII chloride.

Figure 2. The corrosion of iron in 1M HCl in the presence of 10^{-3}M Group VIII chloride.

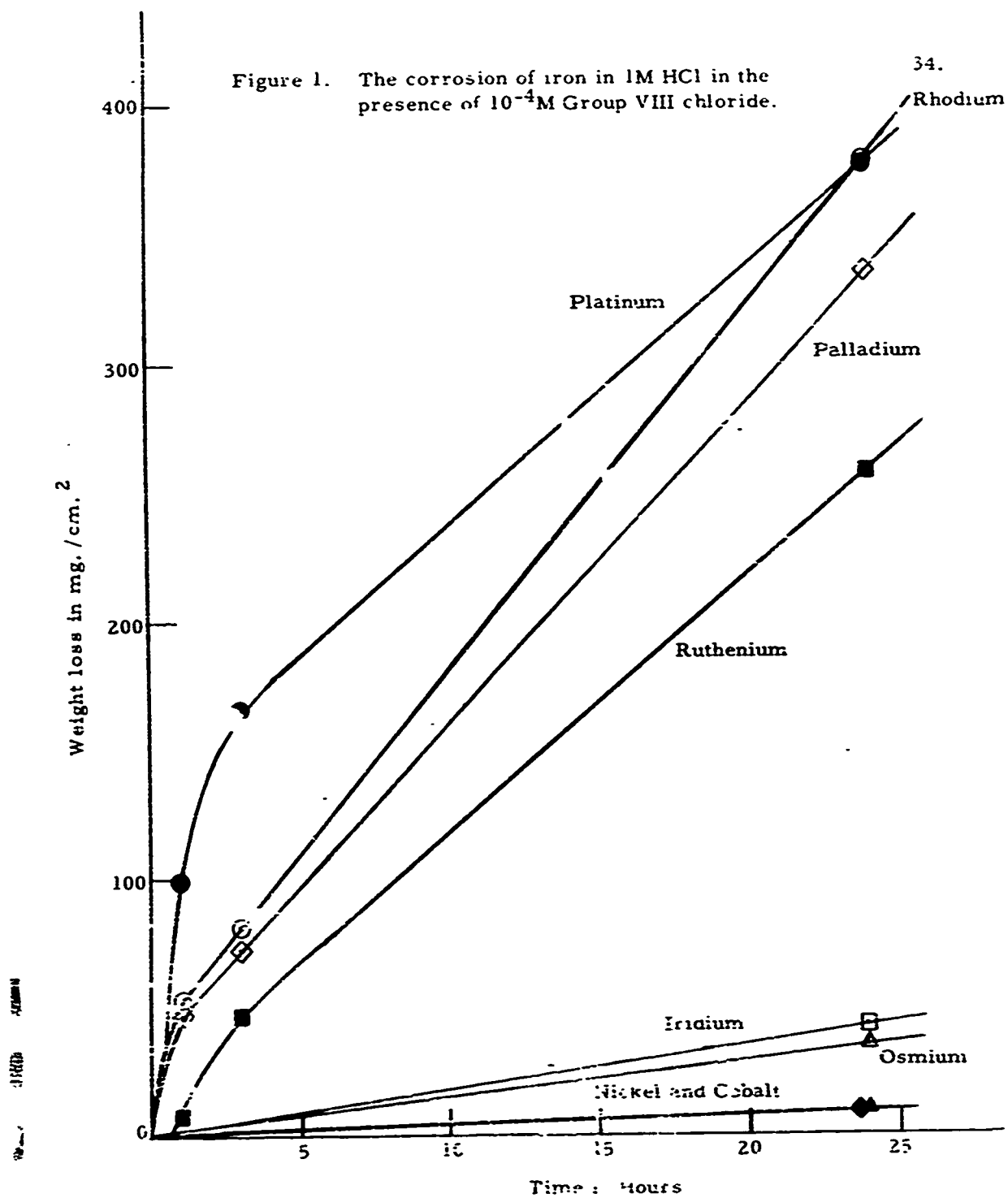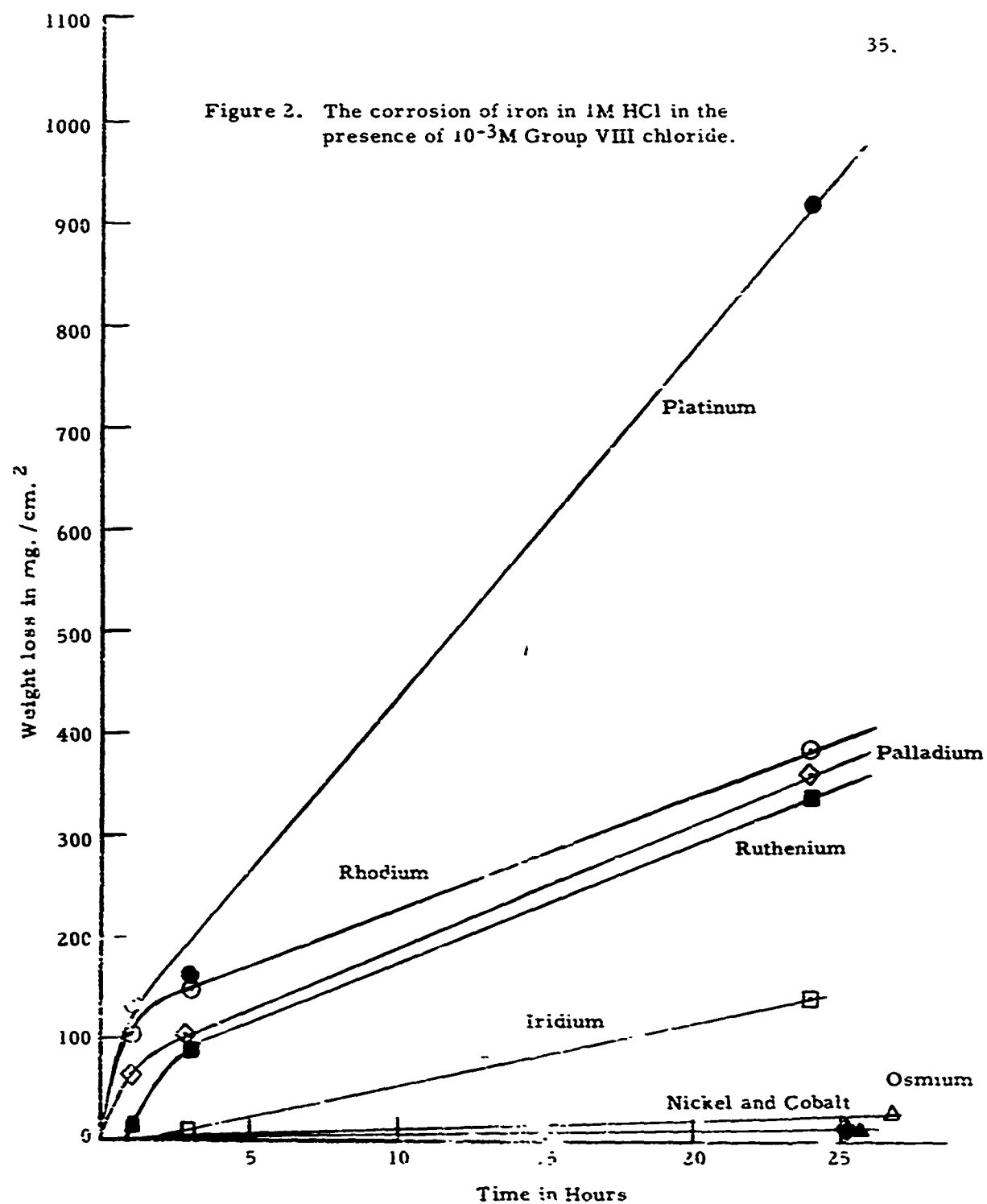Figure 3. The corrosion of iron in 2M HCl in the presence of 10^{-3}M Group VIII chloride.

Figure 4. The corrosion of iron in 2M HCl in the presence of 10^{-3}M Group VIII chloride.
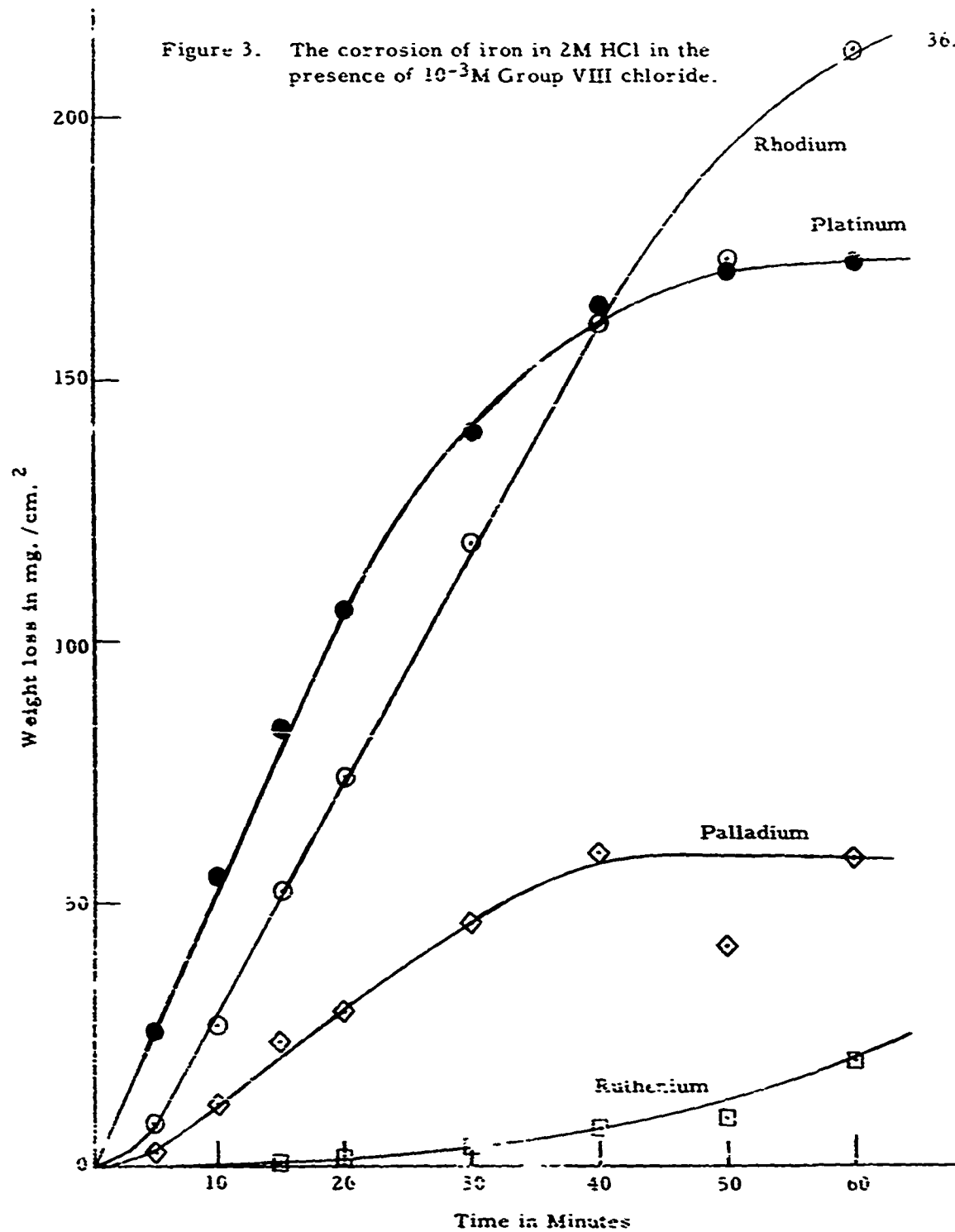
37.
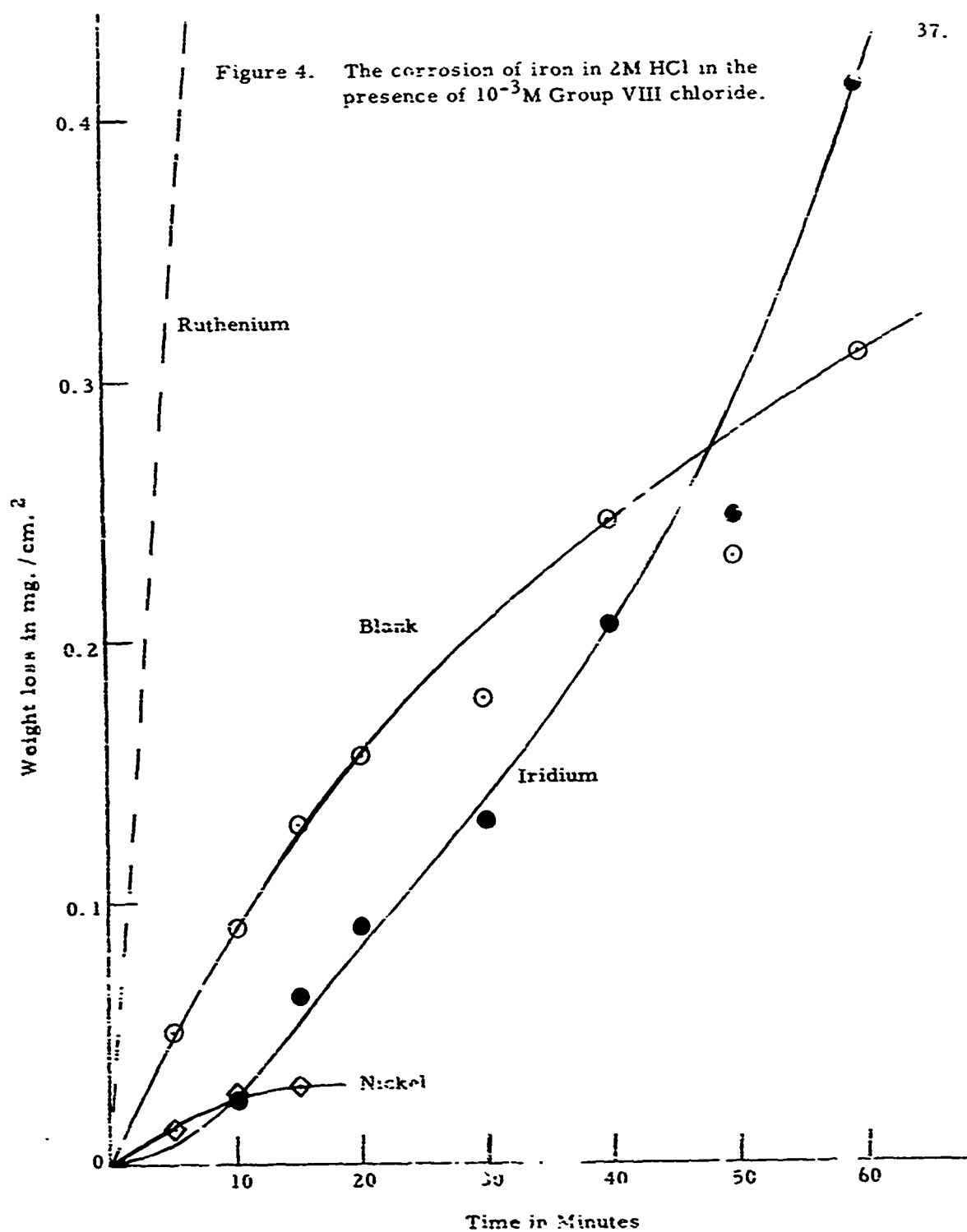
Figure 5. The corrosion of iron in 0.5 M H_2SO_4 in the presence of 10^{-4}M Group VIII chloride.
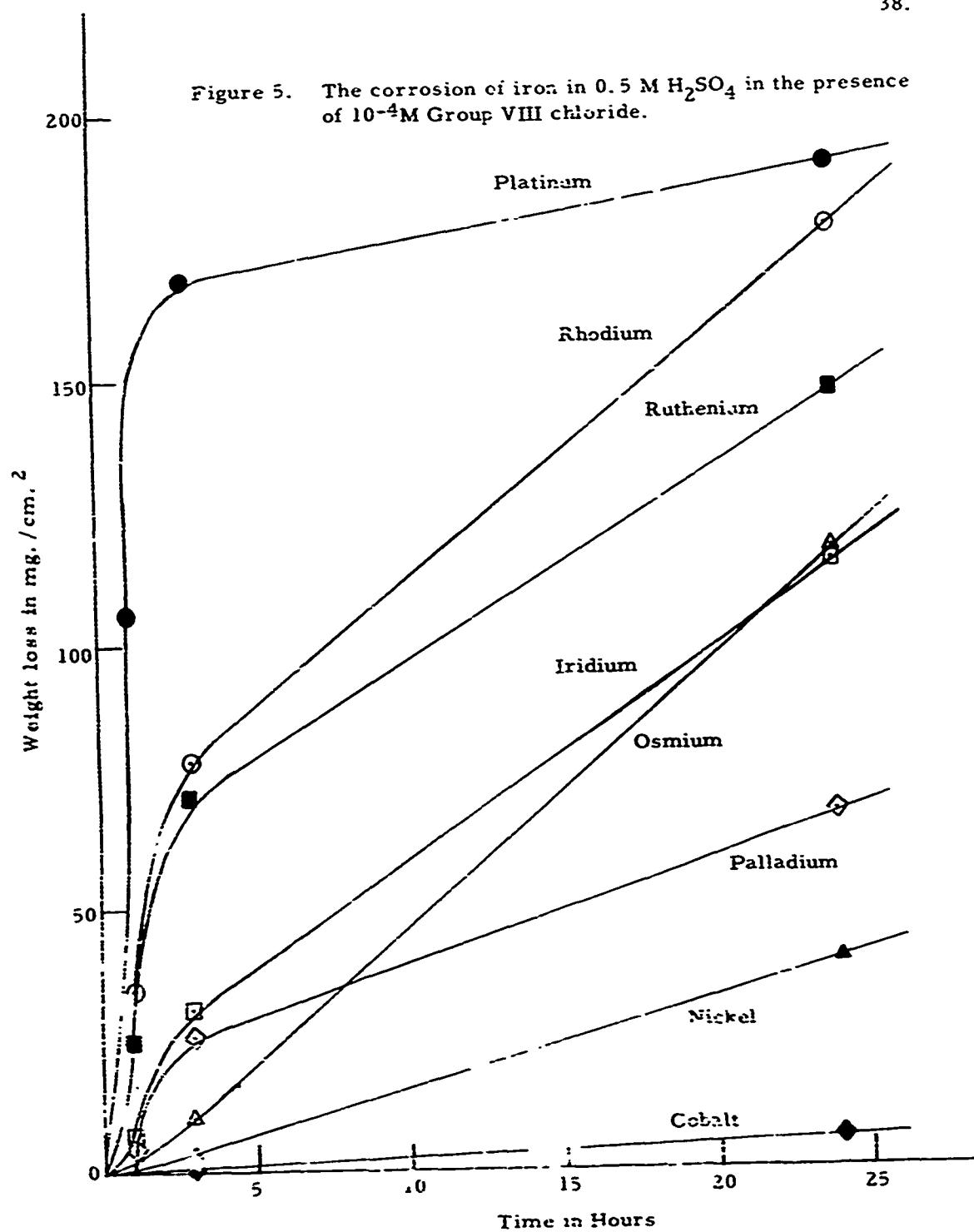
Figure 6. The corrosion of iron in 0.5 M H_2SO_4 in the presence of $10^{-3}M$ Group VIII chloride.
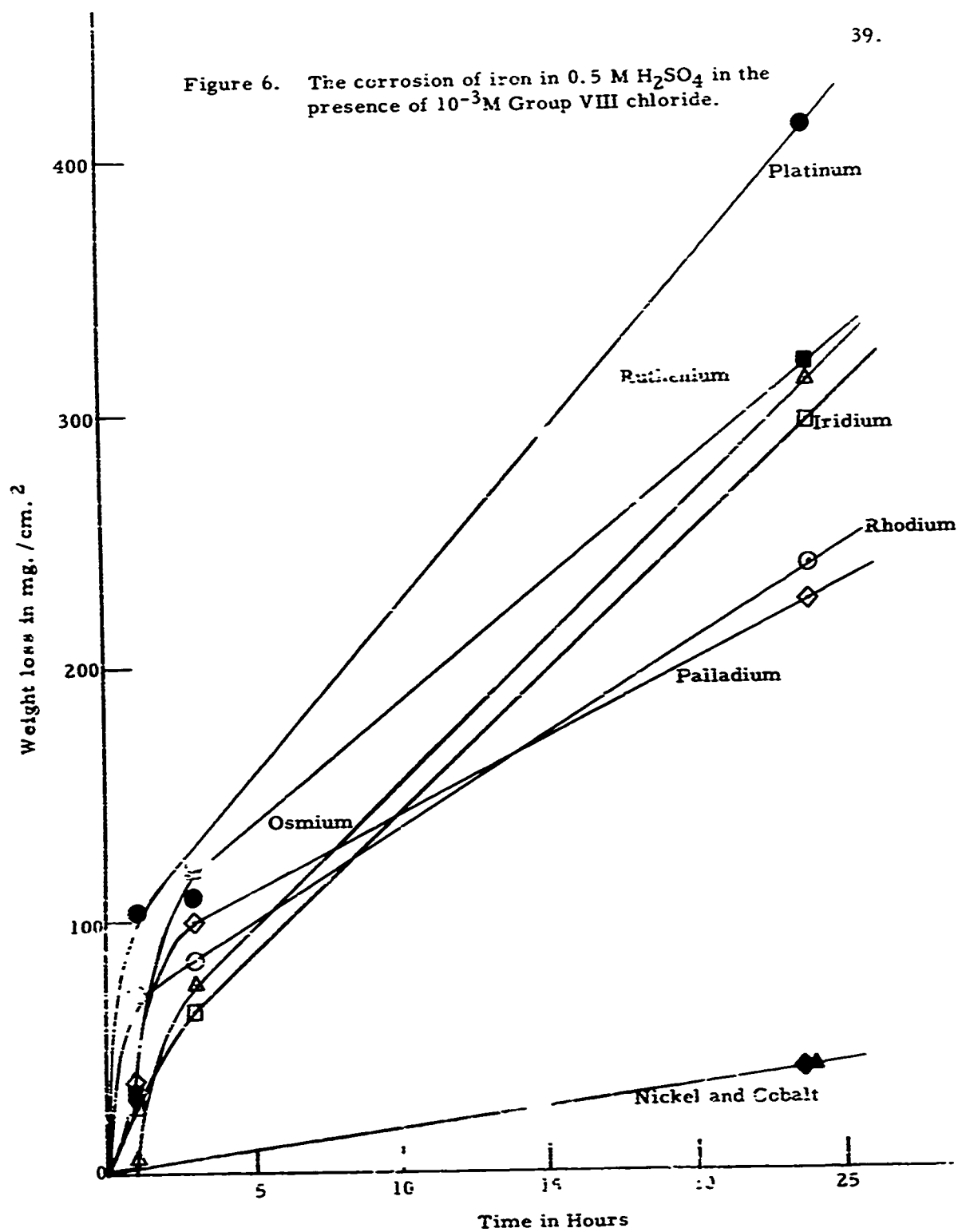
chloride in 1M HCl. Since the rates in the presence of platinum were so great, it was necessary to limit the experiments to one hour. The results of these experiments are summarized in Table I. Experiments with other mixtures are summarized in Tables II - V.

TABLE I

The Corrosion of Iron in 1M HCl at Room Temperature in the Presence of $10^{-3}M$ Each of Two Group VIII Chlorides.

Mixture of $10^{-3}M$ of each	Weight loss in 1 hour in mg./cm.^{2}
Pt and Co	177
Pt and Ni	179
Pt and Ru	177
Pt and Rh	165
Pt and Pd	116
Pt and Os	173
Pt and Ir	177
Pt alone	136

TABLE II

The Corrosion of Iron in 1M HCl at Room Temperature in the
Presence of 10^{-4}M Each of Two Group VIII Chlorides.

Mixture of 10^{-4}M of each	Weight loss in 1 hour in mg./cm.^{2}
Pt and Co	96
Pt and Ni	96
Pt and Ru	90
Pt and Rh	94
Pt and Pd	100
Pt and Os	79
Pt and Ir	89
Pt alone	99

- -

TABLE III

The Corrosion of Iron in 0.5M H_2SO_4 at Room Temperature in
the Presence of 10^{-3}M Each of Two Group VIII
Chlorides.

Mixture of 10^{-3}M of each	Weight loss in 1 hour in mg./cm.^{2}
Pt and Co	109
Pt and Ni	99
Pt and Ru	86
Pt and Rh	75
Pt and Pd	82
Pt and Os	83
Pt and Ir	83
Pt alone	104

TABLE IV

The Corrosion of Iron in 0.5M H_2SO_4 at Room Temperature in the Presence of $10^{-4}M$ Each of Two Group VIII Chlorides.

Mixture of $10^{-4}M$ of each	Weight loss in 1 hour in mg./cm.^{2}
Pt and Co	.55
Pt and Ni	110
Pt and Ru	43
Pt and Rh	44
Pt and Pd	54
Pt and Os	85
Pt and Ir	116
Pt alone	106

TABLE V

The Corrosion of Iron in 2M HCl at Room Temperature in the Presence of $10^{-3}M$ Each of Two Group VIII Chlorides.

Mixture of $10^{-3}M$ of each	Weight loss in 1 hour in mg./cm.^{2}	
	Mixture	Second metal alone
Ru and Co	10	0.5
Ru and Ni	10	0.1
Ru and Rh	186	189
Ru and Pd	128	39
Ru and Os	12	0.5
Ru and Ir	30	0.5
Ru and Pt	317	310
Ru alone	---	10

It was recognized as these experiments were proceeding that rates obtained in the presence of platinum were probably the maximum that could be obtained under the conditions used. It thus became apparent that if any synergistic effect was to be found, it should be sought in systems in which neither of the two species were very active when used singly. Experiments were thus carried out in 2M HCl with mixtures of osmium and cobalt (Figure 7), of osmium and nickel (Figure 8), and of iridium with osmium, cobalt, and nickel (Figure 9). It will be noted that in all cases the rate of corrosion in the presence of the two metals was greater than the sum of their effects singly. Additional experiments must be carried out to confirm this observation and to determine why this is true.

Figure 7. The corrosion of iron in 2M HCl in the presence of 10^{-3}M Group VIII chloride.

Osmium plus Cobalt

Cobalt and Osmium

Weight loss in mg./cm.^{2}

Time in Minutes

Figure 8. The corrosion of iron in 2M HCl in the presence of 10^{-3}M Group VIII chloride.

45.

Figure 9. The corrosion of iron in 2M HCl in the presence of 10^{-3}M Group VIII chlorides.
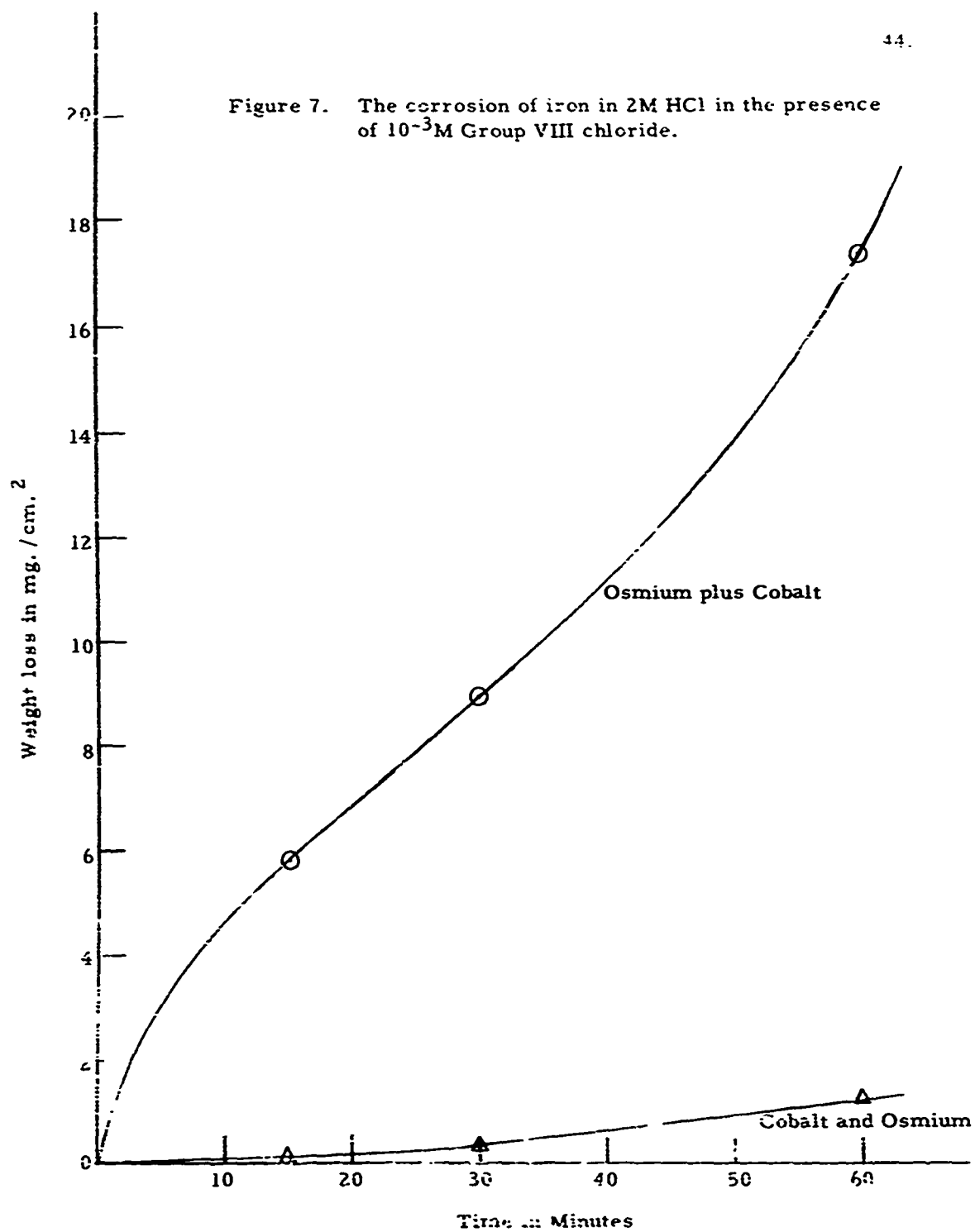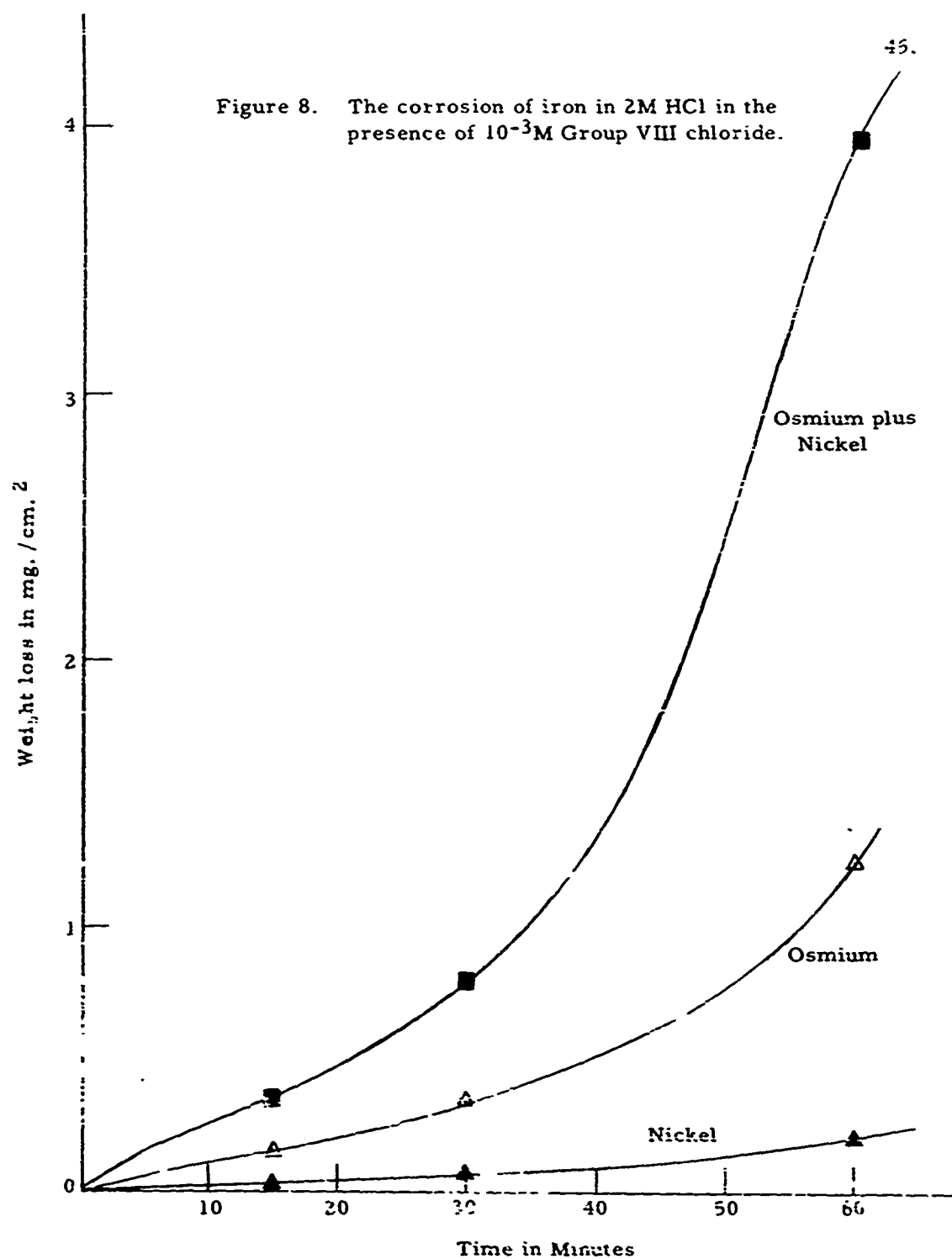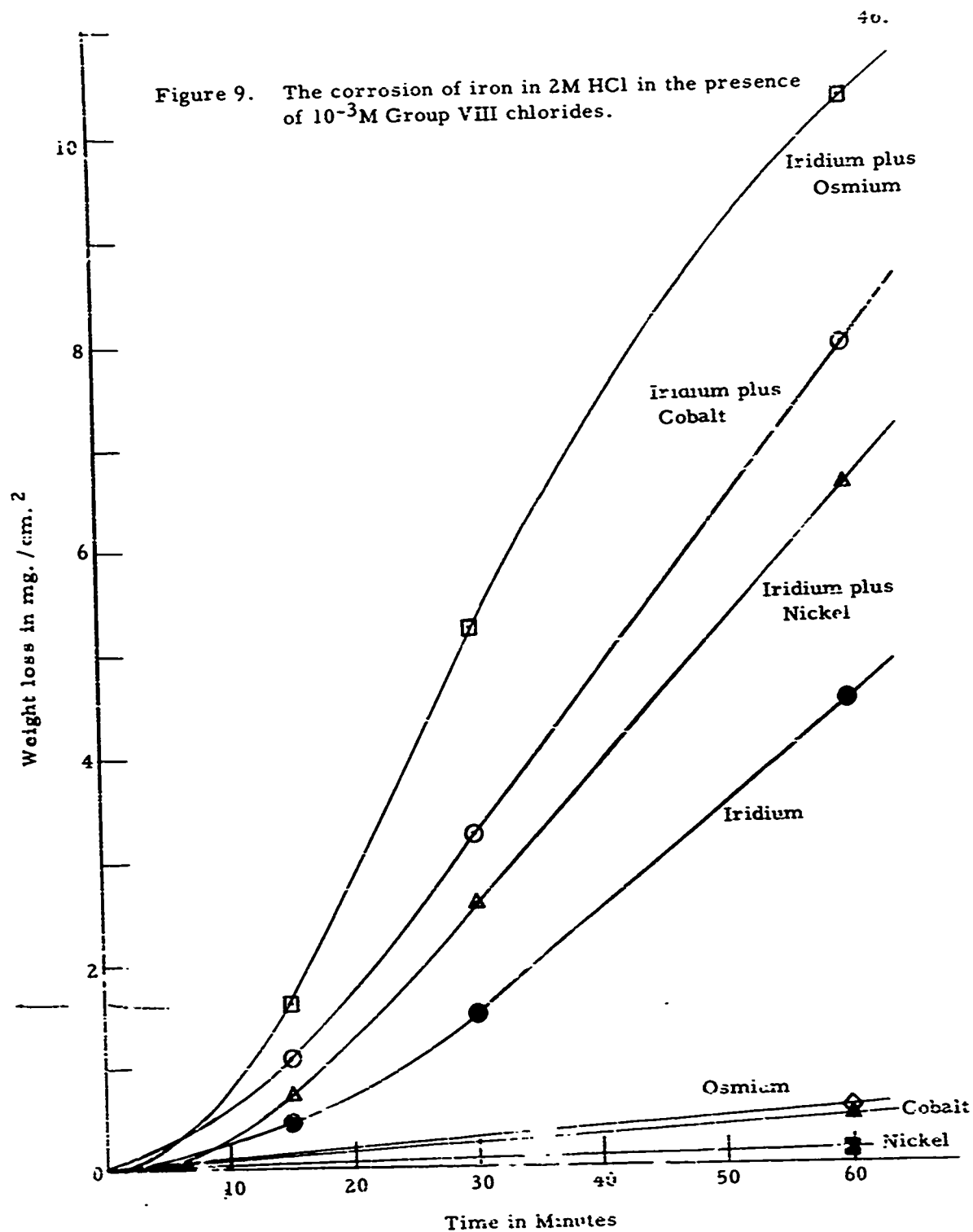
Corrosion in the Presence of Platinum Chloride and an Inert Salt. The rate of corrosion of iron was determined in 2M HCl containing approximately a 2M concentration of an inert salt and 10^{-3}M platinum chloride. The results of this study are given in Table VI.

TABLE VI

Effect of the Addition of an Inert Salt to a Concentration of Approximately 2M on the Corrosion of Iron in 2M HCl Containing 10^{-3} Platinum Chloride

	Weight loss in mg./cm.^{2}		
Added Salt	1 hour	3 hours	24 hours
Blank (10^{-3}M Pt)	310	449	1001
LiF	58	104	245
NaF	2.95	4.1	14.4
KF	0.013	sl. gain	0.49
LiCl	155	270	942
NaCl	142	208	948
KCl	22	143	397
NaBr	177	274	858
LiI	146	143	827
NaI*	2.1	13.7	464
Al$_2$(SO$_4$)$_3$	79	120	519

* - Corrosion in this case was by pitting and by dislodgement of fragments which fell to bottom of flask.

Corrosion in A___ _s Containing Both an Activator and an Inhibitor.

Previous experiments have shown that platinum is a very effective activator for the corrosion of iron in both mineral and fruit acids (1). It is also well known that certain materials are very effective in inhibiting the corrosion of iron in many cases by the formation of a protective film on the surface. The purpose of these experiments was to determine if a combination of an activating agent, such as platinum, and a film-forming substance, such as $SnCl_2$, might have the net effect of concentrating the attack at a few locations with consequent deep pitting or perforation of the sample. Results obtained in 2N HCl, 2N H_2SO_4, 2N citric acid, and 2N formic acid containing 10^{-4}M $PtCl_4$ in the presence of 0.5M and 0.1M additions of potassium dichromate, sodium iodide, lead chloride, tin chloride, and sodium phosphate are summarized in Tables VII and VIII.

It will be noted from Table VII that the most effective combination of activator and inhibitor, insofar as perforation is concerned, is platinum plus NaI. In fact, in HCl the iron sample was completely perforated in 6 places. When the sample was held up to the light, the perforation was readily observed. Further studies should be carried out using $SnCl_2$ as an inhibitor at a series of concentrations below 0.1M This concentration is apparently too high and almost complete protection was obtained in all four acids. It also appears desirable to carry out additional experiments using other alkali metal halides in place of NaI.

TABLE VII

The Corrosion of Ferrovac Iron in Acids in the
Presence of $10^{-4}M$ PtCl$_4$ and Various Inhibitors at Room
Temperature in 24-Hour Period

Acid	Added Inhibitor	Weight Loss in mg./cm.^{2}	Remarks
2N HCl	0.5M K$_2$Cr$_2$O$_7$	197 mg.	general corrosion with even pitting
	0.5M NaI	990	severe corrosion with complete perforation of sample in 6 places
	0.5M PbCl$_2$	42	some pitting, not severe
	0.5M SnCl$_2$	nil	several small pits
	0.5M Na$_3$PO$_4$	545	general corrosion with large, shallow pits
2N H$_2$SO$_4$	0.5M K$_2$Cr$_2$O$_7$	215	uneven corrosion, general pitting
	0.5M NaI	940	uneven corrosion, 12 deep pits
	0.5M PbCl$_2$	222	deep pitting in center
	0.5M SnCl$_2$	nil	no pitting
	0.5M Na$_3$PO$_4$	990	even corrosion with 12 pits
2N citric	0.5M K$_2$Cr$_2$O$_7$	nil	no corrosion or pitting
	0.5M NaI	315	rough surface, 8 pits
	0.5M PbCl$_2$	nil	no corrosion or pitting
	0.5M SnCl$_2$	nil	no corrosion or pitting
	0.5M Na$_3$PO$_4$	55	about 12 small pits
2N formic	0.5M K$_2$Cr$_2$O$_7$	nil	no corrosion or pitting
	0.5M NaI	380	rough surface, 15 pits

TABLE VII (cont.)

Acid	Added Inhibitor	Weight Loss in mg. /cm.^{2}	Remarks
2N formic	0.5M PbCl$_2$	35	Pb deposited out
	0.5M SnCl$_2$	nil	no corrosion or pitting
	0.5M Na$_3$PO$_4$	162	no pitting

TABLE VIII

The Corrosion of Ferrovac Iron in Acids in the
Presence of $10^{-4}M$ PtCl$_4$ and Various Inhibitors at Room
Temperature in 24-Hour Period

Acid	Added Inhibitor	Weight Loss in mg./cm.^{2}	Remarks
2N HCl	0.1M K$_2$Cr$_2$O$_7$	475	general corrosion, even pitting
	0.1M NaI	350	rough surface, uneven pitting
	0.1M PbCl$_2$	40	small, scattered pits
	0.1M SnCl$_2$	1.2	a few small pits
	0.1M Na$_3$PO$_4$	860	general corrosion, large pits
	blank	955	general corrosion, large pits
2N H$_2$SO$_4$	0.1M K$_2$Cr$_2$O$_7$	68	general corrosion, fine pits
	0.1M NaI	220	uneven pitting
	0.1M PbCl$_2$	178	uneven pitting
	0.1M SnCl$_2$	2.2	no pitting
	0.1M Na$_3$PO$_4$	530	general corrosion, medium-size pits
	blank	325	general corrosion, large and medium-size pits
2N citric	0.1M K$_2$Cr$_2$O$_7$	42	fine pits
	0.1M NaI	133	medium pits
	0.1M PbCl$_2$	nil	no corrosion

TABLE VIII (cont.)

Acid	Added Inhibitor	Weight Loss in mg /cm.^{2}	Remarks
	0. 1M $SnCl_2$	nil	no corrosion
	0. 1M Na_3PO_4	81	fine pits
	blank	99	fine pits
2N formic	0. 1M $K_2Cr_2O_7$	89	fine pits
	0. 1M NaI	71	20 medium pits
	0. 1M $PbCl_2$	0.5	no pitting
	0. 1M $SnCl_2$	nil	no corrosion
	0. 1M Na_3PO_4	53	very fine pits
	blank	220	medium pits

Corrosion in Organic Acids. Results are summarized in Table IX for experiments carried out for 3 hours in 2N acids containing 10^{-3}M added Group VIII metal. Table X summarizes similar experiments for an immersion time of 24 hours and includes results for distilled water and 2N sodium chloride solution.

Rapid rates of corrosion were obtained in malic, formic, citric, and acetic acids and a low rate of corrosion was obtained in oxalic acid. The latter result is presumably attributable to the low solubility of ferrous oxalate.

TABLE IX

The Effect of 10^{-3}M Group VIII Metal Ions on the Corrosion of Iron in 2N Organic Acids

Total immersion time: 3 hours   Corrosion rates listed in mg. Fe/cm.^{2}/hr.

Metal Ion	Malic	Formic	Oxalic	Citric	Acetic
Blank	0.066	0.15	neg.	0.026	0.053
Co	0.033	0.14	neg.	0.79	0.04
Ir	1.8	1.6	neg.	1.5	1.4
Ni	0.039	0.18	neg.	0.079	0.079
Os	0.50	0.60	neg.	0.32	0.29
Pd	4.3	3.9	neg.	3.6	1.2
Rh	31	2.8	neg.	13	6.4
Ru	0.28	0.25	neg.	0.27	0.51
Pt	21	30	0.19	16	7.5

In general, it will be noted that platinum, rhodium, and palladium were most effective, iridium, osmium, and ruthenium were of intermediate effectiveness, and nickel and cobalt were relatively ineffective. These results agree in a qualitati e way with those obtained previously at the boiling point in 0.2M citric acid (1).

TABLE X

The Effect of 10^{-3}M Group VIII Metal Ions on the Corrosion of Iron in 2N Organic Acids, Distilled H_2O and 2N NaCl

Total immersion time: 24 hours   Corrosion rates listed in mg. Fe/cm.^{2}/hr.

Metal Ion	Malic	Formic	Oxalic	Citric	Acetic	Distilled Water	Sodium Chloride
Blank	0.045	0.11	neg.	0.040	0.12	neg.	neg.
Co	0.053	0.10	neg.	0.032	0.032	0.006	0.001
Ir	2.2	1.8	neg.	1.6	1.9	0.017	0.014
Ni	0.042	0.35	neg.	0.052	0.07i	0.010	0.010
Os	0.56	0.60	neg.	0.66	2.5	0.046	0.042
Pd	2.8	2.2	0.057	2.4	1.8	0.047	0.017
Rh	20	1.7	0.048	5.5	2.0	0.050	0.021
Ru	1.7	0.40	0.079	1.7	1.1	0.039	0.027
Pt	5.1	12	0.090	4.6	3.0	0.12	0.045

The fastest corrosion rate (31.4 mg./cm.^{2}/hr.) was obtained in malic acid containing 10^{-3}M rhodium. The second fastest corrosion rate (4.9 mg./cm.^{2}/hr.) was obtained in formic acid containing 10^{-3}M platinum.

The great acceleration of the corrosion of aluminum by mercury suggested that it might be advisable to determine if the presence of both a platinum metal and mercury in solution would accelerate the corrosion of iron over and above that obtained in the presence of the platinum metal alone.

A series of experiments to test this possibility is summarized in Table XI. The presence of mercury decreased the effectiveness of platinum in malic, formic, citric, and acetic acids, as might be expected since mercury is a well-known poison for the hydrogen evolution reaction. In malic acid, however, the effect of platinum plus mercury was slightly greater than the effect of platinum alone.

TABLE XI

The Effect of 10^{-3} Pt^{+4} Ion and/or $10^{-3}M$ Hg^{+2} Ion on the Corrosion of Iron in 2N Organic Acids
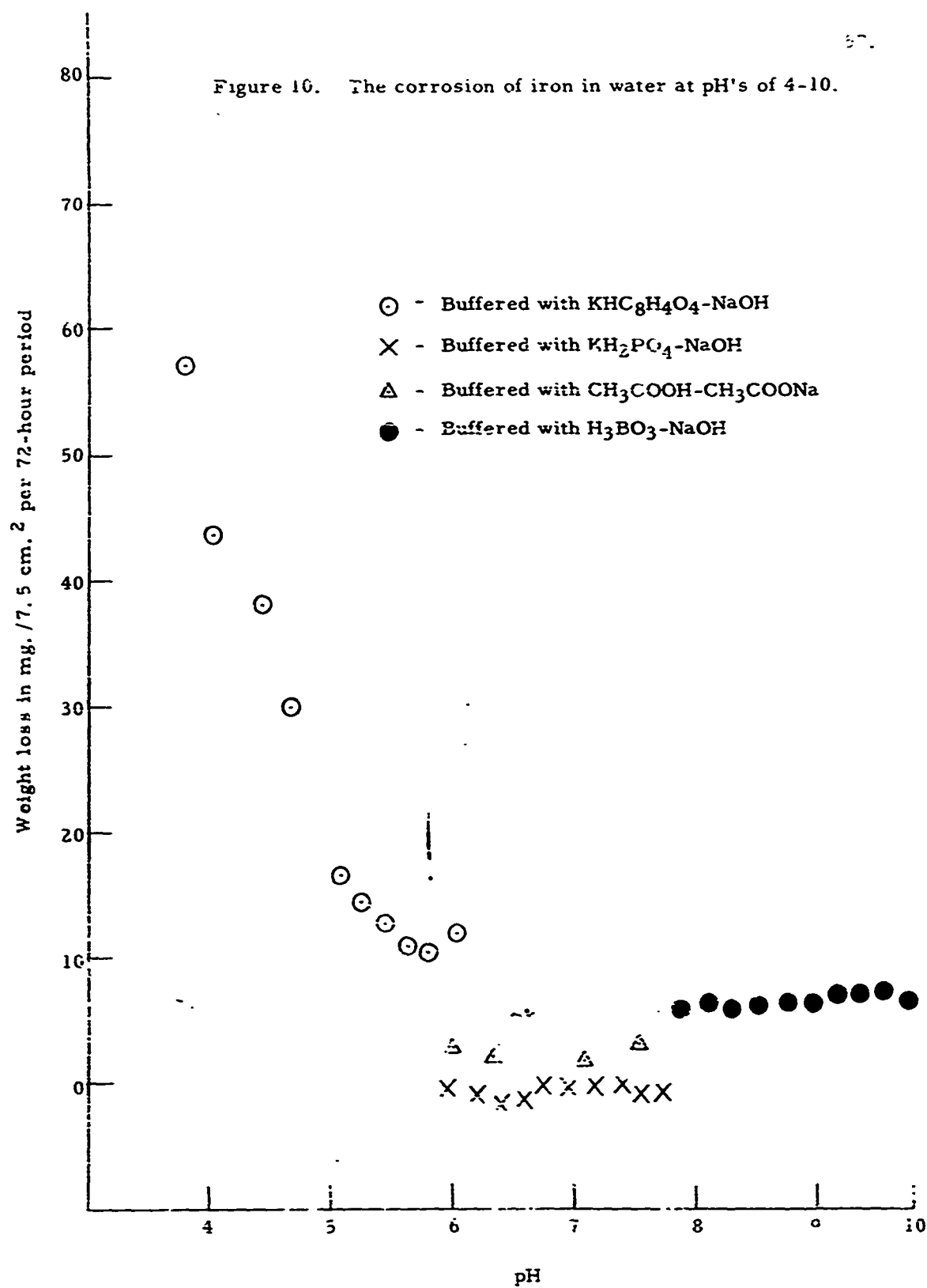
Total immersion time: 3 hours   Corrosion rates listed in mg. $Fe/cm.^2/hr.$

Metal Ion	Malic	Formic	Oxalic	Citric	Acetic
Blank	0.066	0.15	neg.	0.026	0.053
Pt	21	30	0.19	16	7.5
Hg	neg.	neg.	neg.	neg.	neg.
Pt + Hg	25	9.0	0.19	11	5.2

The Corrosion of Iron in the pH Range of 4-10.   A series of experiments was carried out to determine the effect of pH on the corrosion of iron. Uhlig (3) has already made experiments of this type, but it appeared advisable to reproduce these results as a preliminary to experiments of another type. It was felt that future experiments might be carried out in an effort to find an agent which was active in promoting the corrosion of iron at moderate pH's. Specifically, it was considered possible that an agent might be found that would promote the dissolution of iron by water in the same way that mercury salts promote the corrosion of aluminum by water.

Measurements were carried out on cylindrical iron samples, 7.5 cm.^{2} in surface area, and polished in the commercial chemical polishing reagent, MirroFe. The samples were exposed to 100 ml. of a quiescent solution for 72 hours in a water bath thermostated at $30°$. A pH range of 4-6 was obtained with mixtures of $KHC_8H_4O_4$ and NaOH; a range of 6-8 was obtained with mixtures of KH_2PO_4 and NaOH in one case and mixtures of CH_3COOH and CH_3COONa in another case; and a range of 8-10 was obtained with mixtures of H_3BO_3 and NaOH.

The losses in weight of the samples are summarized in Figure 10. Active corrosion of the samples began at pH 6 and increased in amount with decrease in pH. Active rusting began at pH 7.8 with the formation of a reddish-brown coating. Above pH 8.45 the rust had both a brown and green appearance. In the intermediate range of pH 6-8.4 the samples retained their bright appearance particularly in the case of the solutions buffered with phosphate.

Figure 10. The corrosion of iron in water at pH's of 4-10.

⊙ - Buffered with $KHC_8H_4O_4$-NaOH

✕ - Buffered with KH_2PO_4-NaOH

△ - Buffered with CH_3COOH-CH_3COONa

● - Buffered with H_3BO_3-NaOH

Weight loss in mg./7.5 cm.^{2} per 72-hour period

pH

RESULTS WITH ALUMINUM

Five standard aluminum alloys and two samples of pure aluminum were exposed to 2N HCl, HNO_3, and H_2SO_4 containing 10^{-3}M mercury, indium, rhodium, or thallium ions and various mixtures of these. The purpose of these experiments was twofold: (1) to determine if other ions were as effective as mercury in accelerating the corrosion of aluminum and (2) to determine if mixtures yielded any synergistic action.

The results obtained with HCl are summarized in Tables XII and XIII; the results obtained with H_2SO_4 are summarized in Tabl. XIV; and the results obtained with HNO_3 are summarized in Table XV.

Results in 2N HCl. In all but two cases the corrosion rate was greater in the presence of mercury or rhodium ions than the blank rate. The largest increase in rate was observed in the case of 99.999% pure aluminum. Additions of small amounts of indium or thallium ions resulted in corrosion inhibition, except in the case of type 7079-T6 alloy in the presence of indium.

Synergistic action was observed in four instances as denoted by the asterisks. Only in the case of the 99.999% pure aluminum was the effect great enough to be certain that it was outside the ability to reproduce experimental results.

A summary of all the experiments carried out on pure aluminum in 2N HCl are summarized in Table XIII. It will be noted that the most effective single addition was ruthenium. This is in agreement with experimental results published previously on the corrosion of pure aluminum in boiling 2N HCl (1)

TABLE XⅡ

The Effect of Various Metal Ions (10^{-3}M) on the Corrosion of Aluminum
Alloys in 2N HCl

Total immersion time: 1.5 hours   Corrosion rates listed in mg. Al/cm.^{2}/min.

Alloy	Blank	Hg	In	Hg&In	Rh	Rh&Hg	Rh&In	Tl	Tl&Hg
E.C.Hill	0.29	3.0	0.001	1.4	1.7	2.1	1.7	0.002	0.003
7079-T6	2.9	3.2	3.9	2.8	4.0	3.6	3.5	1.3	1.5
5456	3.4	3.5	2.2	2.4	3.0	3.6	3.3	1.5	2.3
360	1.3	1.1	0.19	0.16	2.5	2.5	2.5	0.25	0.025
6101	0.28	1.4	0.002	1.0	1.5	2.0	1.8*	0.011	0.022
2014	2.4	4.7	0.12	0.41	3.3	3.4	3.4	0.21	0.54
R-5-9's	0.001	0.30	neg.	3.4±	1.2	3.3*	1.3	neg.	0.36*

TABLE XIII

The Effect of Various Metal Ions $(10^{-2} M)$ on the Corrosion
of R-5-9's Aluminum in 2N HCl

Total immersion time: 1.5 hours Corrosion rates listed in mg. Al/cm.^{2}/min.

Metal Ion	Corrosion Rate
Blank	0.001
Pt	0.41
Pd	0.30
Os	0.10
Ir	0.090
Fe	0.0091
Co	0.001
Ni	0.004
Ru	3.3
Rh	1.2
Cu	0.26
Hg	0.30
In	neg.
Tl	neg.
Ru&Rh	3.3
Ru&Hg	1.2
Ru&In	3.2
Rh&In	1.3
Cu&Ru	3.4
Cu&Rh	1.6*
Cu&Hg	1.1*
Cu&In	0.086
Hg&In	3.4*
Hg&Rh	3.3*
Hg&Tl	0.36*

TABLE XIV

The Effect of Various Metal Ions ($10^{-3}M$) on the Corrosion of Aluminum
Alloys in 2N H_2SO_4

Total immersion time: 1.5 hours Corrosion rates listed in mg. Al/cm.^{2}/min.

Alloy	Blank	Hg	In	Hg&In	Rh	Rh&Hg	Rh&In
E.C.Hill	neg.	0.37	neg.	0.37	0.029	0.001	neg.
7079-T6	neg.	0.23	neg.	0.10	neg.	neg.	neg.
5456	neg.	0.61	neg.	2.1 *	0.14	0.012	0.005
360	neg.	0.039	0.001	0.051	0.005	0.001	0.002
6101	neg.	0.34	neg.	0.71 *	0.040	0.004	neg.
2014	neg.	0.11	0.001	0.008	0.002	0.001	0.002
R-5-9's	neg.	0.23	neg.	2.0 *	0.031	0.001	neg.

TABLE XV

The Effect of Various Metal Ions ($10^{-3}M$) on the Corrosion of Aluminum
Alloys in 2N HNO_3

Total immersion time: 1.5 hours Corrosion rates listed in mg. Al /cm.^{2}/min.

Alloy	Blank	Hg	In	Hg&In	Rh	Rh&Hg	Rh&In
E.C.Hill	neg.	2.8	0.001	1.2	0.001	0.002	0.002
7079-T6	neg.	0.096	0.001	0.13	neg.	0.002	0.002
5456	neg.	0.045	0.003	0.20*	0.002	0.003	0.003
360	neg.	0.076	0.003	0.10	0.002	0.002	0.003
6101	neg.	3.0	0.001	1.0	neg.	0.002	0.002
2014	neg.	0.029	0.004	0.055	0.002	0.003	0.003
R-5-9's	neg.	0.99	neg.	1.3 *	0.001	0.002	0.002

Results in 2N H_2SO_4. In general, the aluminum alloys were much less susceptible to corrosion in H_2SO_4 than in HCl. Additions of mercury or rhodium ions increased the rate of corrosion of all alloys. The largest increase in corrosion in a system containing only a single additive was observed with the 5456 alloy in the presence of mercury ions. Indium ions alone appeared ineffective. Three cases of synergistic action were noted, all with mixtures of mercury and indium ions. The greatest synergistic action took place with the high purity aluminum where there was a 10-fold increase over the added rates in the presence of mercury and indium ions alone.

Results in 2N HNO_3. The purer aluminum samples (R-5-9's, E. C. Hill, and type 6101) were particularly susceptible to attack in HNO_3 in the presence of mercury ions. However, indium or rhodium ions, indium plus rhodium ions, and rhodium plus mercury ions were less effective in HNO_3 than in HCl or H_2SO_4 for all alloys. Synergistic action, as noted by the asterisks in Table XIV, was observed in two cases.

Results in distilled water and 2N NaCl. A few experiments, summarized in Tables XVI and XVII, were carried out in distilled water and 2N NaCl in the presence of mercury and indium ions. The corrosion rates were very low compared to the rates in the mineral acids but they were still appreciable. For example, the R-5-9's aluminum exhibited a corrosion rate of 0.020 mg./cm.2/min. in the presence of 10^{-3}M each of mercury and indium. This rate is equivalent to a weight loss of 29 mg /cm.2 during a 24-hour period

TABLE XVI

The Effect of 10^{-3}M Hg^{+2} Ion and/or 10^{-3}M In^{+3} Ion on the Corrosion of
Aluminum Alloys in 2M NaCl

Total immersion time: 24 hours Corrosion rates listed in mg. Al/cm.^{2}/min.

Alloy	Blank	Hg	In	Hg&In
E. C. Hill	neg.	0.017	neg.	0.005
7079-T6	neg.	neg.	neg.	0.001
5456	neg.	0.006	neg.	0.003
360	neg.	neg.	neg.	0.001
6101	neg.	0.019	neg.	0.005
2014	neg.	neg.	neg.	0.001
R-5-9's	neg.	neg.	neg.	neg.

TABLE XVII

The Effect of 10^{-3}M Hg^{+2} Ion and/or 10^{-3}M In^{+3} Ion on the Corrosion of
Aluminum Alloys in Distilled Water

Total immersion time: 24 hours Corrosion rates listed in mg. Al/cm.^{2}/min.

Alloy	Blank	Hg	In	Hg&In
E. C. Hill	neg.	0.009	neg.	0.006
7079-T6	neg.	0.012	neg.	0.005
5456	neg.	0.003	neg.	0.008
360	neg.	neg.	neg.	<0.001
6101	neg.	0.022	neg.	0.019
2014	neg.	neg.	neg.	0.001
R-5-9's	neg.	0.018	neg.	0.020

<u>The Effect of Temperature on the Corrosion of Aluminum in 2N HCl</u>

<u>in the presence of Mercury and/or Rhodium.</u>   These measurements were

carried out on cylinders of 99.999% aluminum each exposing 5-6 cm.[2]

Constant temperature was maintained by means of a thermostated water

bath. Mercury and rhodium chlorides were added to a concentration of

10^{-3}M each. The amount of corrosion was determined by weight loss

measurements.

Measurements made in 2N HCl containing 10^{-3}M Hg(II) are summa-

rized in Table XVIII. Measurements made in 2N HCl containing 10^{-3}M

Rh(III) are summarized in Table XIX. Measurements made in 2N HCl con-

taining both 10^{-3}M Hg(II) and 10^{-3}M Rh (III) are summarized in Table V.

TABLE XVIII

The Corrosion of 99.999% Aluminum in 2N HCl Containing
10^{-3}M HgCl$_2$ (All Values in mg./cm.[2])

Time in minutes	Temperature in °C.							
	10°	20°	30°	40°	50°	60°	70°	80°
5	---	---	---	---	---	1.5	8.1	10.5
10	---	---	1.9	6.8	3.9	6.9	15.3	22.1
15	11.8	—	13.9	4.1	14.4	15.9	34.3	35.7

TABLE XIX

The Corrosion of 99.999% Aluminum in 2N HCl Containing
10^{-3}M RhCl$_3$ (All Values in mg./cm.^{2})

Time in minutes	Temperature in °C.							
	10°	20°	30°	40°	50°	60°	70°	80°
5	75	93	102	107	105	111	96	98
10	113	127	131	123	115	118	108	93
15	143	150	143	120	130	110	105	91

TABLE XX

The Corrosion of 99.999% Aluminum in 2N HCl Containing
10^{-3}M HgCl$_2$ and 10^{-3}M RhCl$_3$ (All Values in mg./cm.^{2})

Time in minutes	Temperature in °C.							
	10°	20°	30°	40°	50°	60°	70°	80°
5	39	51	63	55	75	101	70	119
10	108	84	100	88	130	114	168	125
15	88	111	182	108	125	142	154	130

The Effect of Stress on the Rate of Corrosion of Aluminum in 2N HCl

in the Presence of Rhodium and/or Mercury. The rates of corrosion of

aluminum in hydrochloric acid in the presence of rhodium and in the presence

of rhodium and mercury were so high that it appeared doubtful that the intro-

duction of stress into the samples would have any appreciable effect on the

corrosion rate. It appeared advisable nonetheless to test this possibility.

Samples of 99.999% aluminum were cut from rods in the form of cylinders, 1/2" in diameter and somewhat greater than 1/4" in length. The length was so chosen that a controlled degree of stress would be introduced into the sample when it was compressed to 1/4" in length. After machining to shape, the samples were lightly etched in HCl and were then heated at 600°C. for 24 hours in order to remove stresses previously introduced in the fabrication process. The samples were next compressed in a punch and die assembly so that they were reduced in size 2.8, 4.7, 6.5, 9.0, 10.7, 13.0, 16.6, and 20.0%. Weight loss measurements were made at 10, 20, 30, 40, 60, and 80° in 2N HCl containing the additive. The results obtained in the presence of 10^{-3}M rhodium are given in Table XXI; those in the presence of 10^{-3}M mercury are given in Table XXII; and those in 10^{-3}M rhodium plus 10^{-3}M mercury are given in Table XXIII.

TABLE XXI

The Weight Loss in a 10-Minute Period of Stressed
99.999% Aluminum in 2N HCl Containing 10^{-3}M RhCl$_3$
(All Values in mg./cm.^{2})

Stress - Represented as % reduction in sample thickness	Temperature					
	10°	20°	30°	40°	60°	80°
0%	127			132		111
2.8					'27	
4.7			142			
6.5					125	
9.0				126		
10.7		132				108
13.0	113				121	
16.6			133			
20.0	111			117		97

TABLE XXII

The Weight Loss in a 10-Minute Period of Stressed
99.999% Aluminum in 2N HCl Containing 10^{-3}M $HgCl_2$
(All Values in mg./cm.^{2})

Stress - Represented as % reduction in sample thickness	Temperature					
	10°	20°	30°	40°	50°	80°
0%				1.2		
2.8					5.3	
4.7						12.6
6.5					3.8	
9.0				0.4		
10.7		2.6				
13.0					4.7	
16.6						
20.0				5.0		

TABLE XXIII

The Weight Loss in a 10-Minute Period of Stressed 99.999%
Aluminum in 2N HCl Containing 10^{-3}M RhCl$_3$ and 10^{-3}M HgCl$_2$
(All Values in mg./cm.^{2})

Stress - Represented as % reduction in sample thickness	Temperature					
	10°	20°	30°	40°	60°	80°
0%				155		
2.8	64				16ʹ	
4.7			124			136
6.5		113			162	
9.0	84			135		
10.7		108				93
13.0	82				135	
16.6			107			
20.0				125		

RESULTS WITH COPPER

<u>Corrosion in 1M H_2SO_4 in the Presence of $10^{-4}M$ Group VIII Chloride.</u>
The results of these experiments are summarized in Table XXIV. In all cases
the rate of corrosion was slightly greater than that of the blank, but in no case
was there a large rate of corrosion. The increased rate over the blank is probably
a result of the dissolution of a small amount of copper by a metal replacement
reaction.

<u>Corrosion in 1M H_2SO_4 in the Presence of $10^{-3}M$ Group VIII Chloride.</u>
The results of these experiments are summarized in Table XXV. In no case
was a large rate of corrosion observed. In all cases the presence of the Group
VIII chloride in the acid caused a slight increase in the rate of corrosion.

<u>Corrosion in 2M HCl in the Presence of $10^{-3}M$ Group VIII Chloride.</u>
The results of these experiments are summarized in Table XXVI. In no case
was a large rate of corrosion observed. In all cases the presence of the Group
VIII chloride in the acid caused a slight increase in the rate of corrosion.

<u>Corrosion in 2M HNO_3 in the Presence of $10^{-4}M$ Group VIII Chloride.</u>
The results of these experiments are summarized in Table XXVII. The copper
corroded, as is well known, at an appreciable rate in the 2M HNO_3 in the ab-
sence of any additive. In all cases the presence of the Group VIII chloride
reduced the rate, with the effective degree of inhibition decreasing in the order:
Pd, Pt, Rh, Ru, Co, Ir, Os, Ni.

With the exception of the experiments with additions of palladium or
platinum, the corrosion rate increased with time. This phenomenon is well

known and has been attributed (4) to the catalytic effect of the nitrogen oxides which are a product of the reaction.

Corrosion in 2M HNO_3 in the Presence of 10^{-3}M Group VIII Chloride.
The results of these experiments are summarized in Table XXVIII. Palladium, platinum, rhodium, cobalt, and nickel additions were effective in decreasing the rate of corrosion. Iridium, ruthenium, and osmium additions reduced the corrosion rate slightly but to no major extent. No cases were found in which the corrosion rate was increased.

TABLE XXIV

The Corrosion of Copper in 1M H_2SO_4 at Room Temperature in the Presence of 10^{-4}M Group VIII Chlorides

Group VIII Chloride	Average Corrosion Rate over a 24-Hour Period (mg. /cm. ^{2}/hr.)
Co	0.014
Ni	0.017
Ru	0.014
Rh	0.022
Pd	0.018
Os	0.019
Ir	0.017
Pt	0.021
Blank	0.007

TABLE XXV

The Corrosion of Copper in 1M H_2SO_4 at Room Temperature in the Presence of 10^{-3}M Group VIII Chlorides

Group VIII Chloride	Average Corrosion Rate over a 24-Hour Period (mg. / m.^{2}/hr.)
Co	0.010
Ni	0.017
Ru	0.016
Rh	0.014
Pd	0.045
Os	0.017
Ir	0.013
Pt	0.035
Blank	0.006

TABLE XXVI

The Corrosion of Copper in 2M HCl at Room Temperature in the Presence of 10^{-3} M Group VIII Chlorides

Group VIII Chloride	Average Corrosion Rate over a 24-Hour Period (mg. /cm.^{2}/hr.)
Co	0.029
Ni	0.026
Ru	0.052
Rh	0.056
Pd	0.034
Os	0.043
Ir	0.029
Pt	0.077
Blank	0.021

TABLE XXVII

The Corrosion of Copper in 2M HNO_3 at Room Temperature in the
Presence of 10^{-4}M Group VIII Chlorides

Group VIII Chloride	Corrosion in mg./cm.^{2}		
	1 Hr.	3 Hrs.	24 Hrs.
Co	1.1	5.0	149
Ni	1.0	5.9	246
Ru	2.0	2.8	130
Rh	0.2	1.3	45
Pd	0.1	0.4	0.8
Os	0.7	5.0	238
Ir	0.8	4.7	160
Pt	0.8	2.1	19
Blank	1.6	9.5	247

TABLE XXVIII

The Corrosion of Copper in 2M HNO_3 at Room Temperature in the
Presence of 10^{-3}M Group VIII Chlorides

Group VIII Chloride	Average Corrosion Rate over a 24-Hour Period (mg./cm.^{2}/hr.)
Co	0.014
Ni	0.014
Ru	6.1
Rh	0.062
Pd	0.044
Os	6.0
Ir	2.0
Pt	0.051
Blank	9.3

DISCUSSION

The great effectiveness of the more noble Group VIII metals in accelerating the corrosion of iron in HCl, H_2SO_4, and 4 organic acids has been amply demonstrated in these experiments. Under the conditions used, the rate in the presence of platinum was as much as 1000 times that of the blank. It has been known for many years that contact of a less noble metal with a low hydrogen overvoltage metal, such as platinum, causes a great increase in the dissolution rate. This increase is attributed to the fact that the cathodic half reaction - the evolution of hydrogen - proceeds at a faster rate on the second metal. Since the cathodic reaction is rate determining in many cases, activation of the cathodic reaction leads to an increased anodic reaction rate. Thus, the Group VIII metal accelerates the overall dissolution reaction by virtue of being a good catalyst for the hydrogen evolution reaction.

The relative activities of the Group VIII chlorides in accelerating the corrosion of iron in the eight media studied are summarized in Table XXIX. It will be noted that platinum was the most effective, rhodium, palladium, iridium and ruthenium were of intermediate effectiveness, and osmium, cobalt, and nickel were least effective. This relative effectiveness agrees well with experiments carried out with iron in boiling 0. 2M citric acid, and cobalt and nickel in boiling 2M HCl. [1] In these experiments the less noble metal was coupled to a cylinder of the platinum metal of equal surface area. The relative effectiveness in those experiments was in the decreasing order: platinum, palladium, rhodium, and iridium.

TABLE XXIX

The Relative Effectiveness of the Group VIII Elements in Accelerating
the Corrosion of Iron in Acids at Room Temperature as Determined
from 1- and 3-Hour Runs.

2M HCl	1M HCl	1M H_2SO_4	0.5M H_2SO_4	2N Malic	2N Formic	2N Citric	2N Acetic
Pt	Pt	Pt	Pt	Rh	Pt	Pt	Pt
Rh	Rh	Ru	Rh	Pt	Pd	Rh	Rh
Pd	Pd	Rh	Pd	Pd	Rh	Pd	Ir
Ru	Ru	Os	Ru	.	Ir	Ir	Pd
Os	Ir	Pd	Ir	Os	Os	Co	Ru
Ir	Os	Ir	Os	Ru	Ru	Os	Os
Co	Co	Co	Co	Ni	Ni	Ru	Ni
Ni	Ni	Ni	Ni	Co	Co	Ni	Co

Average Relative Effectiveness in Eight Media

Platinum - 63 points*

Rhodium - 55

Palladium - 46

Iridium - 35

Ruthenium - 34

Osmium - 29

Cobalt - 15

Nickel - 11

* - Giving 8 points for most active, 7 for 2nd most active etc.

It appears likely in many of the experiments with platinum additions
that diffusion of reaction species to the surface or diffusion of products
away from the surface may have been rate limiting. As shown in Table I
for example, six of the mixtures yielded a weight loss in one hour of 165-
179 mg./cm.^{2} Presumably the rates could have been increased beyond this
range by increasing the rate of diffusion by agitation of the solution.

The most severe type of corrosion of iron was observed in the case
of mineral acids, 10^{-4}M added platinum, and sodium iodide. Pitting of the
samples was very great and, in the case of the sample in 2M HCl, complete
performation occurred. Pitting was also observed in other systems involving
both an activator, such as platinum, and an inhibitor such as Na_3PO_4.

All the aluminum alloys exhibited high rates of corrosion in HCl in the
presence of (a) mercury, (b) rhodium, (c) rhodium plus mercury, and (d)
rhodium plus indium. Ruthenium was also very effective in accelerating the
corrosion of pure aluminum in HCl. Experiments with this additive were not
carried out with all the alloys, however. Additions of mercury alone, or
mercury plus indium, were effective in causing a rather high rate of corrosion
in water or sodium chloride solution.

The experiments summarized in Tables XVII through XXIII indicate
that temperature and degree of stress did not have a very great effect on the
rate of corrosion in the presence of accelerating additives such as mercury
and rhodium These results support the idea that the rate of corrosion under
the conditions used was dependent primarily upon the rate of diffusion of

reactants to or products away from the site of reaction.

No evidence was found for an appreciable increase in the corrosion rate of copper in the presence of dissolved Group VIII transition metal chlorides. This result is to be expected since the Group VIII metals are effective in accelerating the corrosion rates of less noble metals by virtue of their ability to catalyze the cathodic hydrogen evolution reaction. In the case of copper, the reaction $Cu + 2HX = Cu^{++}(aq) + H_2(g) + 2X^-(aq)$, is unfavorable from a thermodynamic point of view in the presence of minute amounts of hydrogen gas. On the other hand, reactions involving the scavenging of hydrogen by oxidizing agents, in which the product of the overall reaction is not gaseous hydrogen, are favored from a thermodynamic viewpoint. In the absence of hydrogen evolution, the platinum metals would not be expected to be effective catalysts for the dissolution reaction.

The most interesting results are those shown in Tables XXVII and XXVIII in which appreciable inhibition of the reaction with HNO_3 was observed. Limiting the analysis to the inert platinum metals, it will be noted that the effectiveness of these metals in inhibiting the corrosion in HNO_3 may be described as follows:

	Effectiveness in Inhibiting the Corrosion in $2M$ HNO_3 at 2 Concentrations of the Pt Metal	
	$10^{-4}M$	$10^{-3}M$
Good Inhibitor	Pd	Pd, Pt, Rh
Moderate Inhibitor	Pt, Rh	none
Poor Inhibitor	Ru, Ir, Os	Ru, Ir, Os

At both concentrations, palladium was the most effective inhibitor, followed by platinum and rhodium. Ruthenium, iridium, and osmium were only slightly effective In previous studies carried out in this laboratory (5) it was hypothesized that good inhibition of the anodic reaction was often ob-tained in reactions with boiling acids under conditions where the inhibiting metal had an appreciable solubility in the corroding metal. For example. palladium is an excellent inhibitor for the corrosion of silver in constant-boiling HCl and copper is an excellent inhibitor for the corrosion of nickel in boiling 2M HCl Palladium-silver and copper-nickel form solid solutions over the entire range of concentration. In the systems used in the present study, the phase diagrams of the copper-palladium and copper-platinum systems indicate complete solid solution over the entire concentration range. In the copper-rhodium system, the solubility of copper in rhodium is of the order of 20 atomic % at room temperature. On the other hand, ruthenium, iridium, and osmium have little or no solubility in copper (6). It is not desired to pursue this analysis too far at the present time until additional critical experiments can be performed.

BIBLIOGRAPHY

(1)   W. Roger Buck, III, and H. Leidheiser, Jr., Corrosion 14, 308
        (1958).

(2)   W. Roger Buck, III, and H. Leidheiser, Jr. , Nature 181, 1681
        (1958).

(3)   H. H. Uhlig, Corrosion Handbook, John Wiley and Sons, p. 129
        (1948).

(4)   U. R. Evans, The Corrosion and Oxidation of Metals, Edward
        Arnold, Ltd., p. 326 (1960).

(5)   H. Leidheiser, Jr., and W. Roger Buck. III, "Contributions to an
        Understanding of Corrosion Inhibition through Experiment with
        Metallic Cations," a paper presented before the Association of
        Corrosion Engineers in Dallas, Texas, March, 1966.

(6)   M. Hansen, Constitution of Binary Alloys, McGraw-Hill Book Co.,
        (1958).

PART C

"The Rapid Corrosion of Metals at Room Temperature in
the Presence of Hydrogen Sulfide, Various Salts, and
Water Vapor"

By

W. Roger Buck, III, and Henry Leidheiser, Jr.

ABSTRACT

Copper, nickel, iron, cadmium, tin, and zinc were rapidly corroded at room temperature in contact with $AgNO_3$ in an atmosphere of H_2S and water vapor. Copper was also rapidly corroded in the presence of $Hg(NO_3)_2$, H_2S, and water vapor. At low concentrations of $AgNO_3$, the weight loss of copper and nickel (the other metals were not studied) was appreciably greater than could be accounted for on the basis of an oxidation-reduction reaction in which the nitrate ion was converted to NO.

INTRODUCTION

The broad purpose of the experimental program covered in this report was to make studies of systems of metal plus environment in which very rapid deterioration of the metal occurs at room temperature. Other portions of this report are concerned with the effect of liquid metals on the cracking and oxidation of metals, the effect of mercury salts on the oxidation of aluminum, and the effect of platinum metals in accelerating the dissolution of metals in aqueous solutions. This portion of the report is concerned with the effect of a gaseous compound, hydrogen sulfide, in accelerating corrosion.

It is well known that hydrogen sulfide has the effect of increasing the rate of oxidation of copper. The initial motivation for the experiments was to choose a system based on copper and hydrogen sulfide at room temperature for quantitative investigation. As the work progressed, it because apparent that many solid salts were extremely corrosive to a number of metals in short periods of time in the presence of hydrogen sulfide and moist air. The experiments reported herein are thus a preliminary appraisal of the effectiveness of hydrogen sulfide in accelerating the corrosion of metals at room temperature in the presence of various salts. Quantitative, more sophisticated experiments were not carried out because the contract was terminated as these experiments were to begin. The need for such quantitative experiments will be apparent as the report is read.

EXPERIMENTAL PROCEDURE

The metals used in this study were the same as those described in the section concerned with deterioration of metals in the presence of liquid metals (Part A). The metals were used in the form of cylinders, 3/8 to 5/8" in diameter. They were degreased after machining and were etched immediately prior to use in 6N hydrochloric acid or dilute nitric acid.

All experiments were carried out in a plastic reaction chamber, 12" x 12" x 5-1/4", which was equipped with a fan for keeping the atmosphere in continuous motion. A relative humidity of 100% was maintained by means of a tray of water placed immediately below the fan. Hydrogen sulfide was generated by immersing small pellets of Na_2S in acetic acid. The partial pressure of hydrogen sulfide in the moist air was not controlled but its average value during the period of the experiment was estimated to be of the order of 150 mm.

EXPERIMENTAL RESULTS

Experiments with Copper

The rapid rate of corrosion of copper in the presence of a mercury salt, H_2S, and moist air is shown by the results in Table I. It next appeared of interest to determine if all three constituents were necessary for this rapid corrosion. As shown in Table II the copper samples exposed to a mercury salt and water vapor at 100% relative humidity did not exhibit any appreciable corrosion. In all cases the samples gained in weight as a result of amalgamation. Table III shows a similar set of experiments in which the samples were exposed to mercury salts and H_2S for 70 hours in an atmosphere which had been freed of the major amount of water vapor by drying with the absorbent, calcium chloride.

It was next of interest to determine if simultaneous attack by the mercury salt and hydrogen sulfide was necessary. In order to test this point copper samples were thoroughly amalgamated by covering them with either $HgSC_4$ or $Hg(NO_3)_2$ and the samples were then transferred to the reaction chamber where they were exposed to H_2S vapor at 100% relative humidity for 22 hours. It will be noted from Table IV that weight losses of only 3 to 11 mg. were observed under these conditions.

The effectiveness of $Hg(NO_3)_2$ in promoting the corrosion of copper suggested that other metallic nitrates should be investigated. Table V summarizes the results obtained with a series of metal nitrates. It will be noted that $AgNO_3$ was by far the most effective in causing severe corrosion of copper.

TABLE I

The Corrosion of Copper in Contact with Mercury Salts in
as Atmosphere of H_2S at 100% Relative Humidity

Mercury Salt (Unweighed)	Loss in Weight of Copper (in mg.)				
	1 Hr.	3 Hrs.	6 Hrs.	22 Hrs.	70 Hrs.
$Hg(NO_3)_2 \cdot H_2O$	42	86	129	1.3	3.7
	188	(2)	139	12.	46.
	125	(40)	136	169	404
	(41)	47		159	337
	31	16			
	21	17			
	16	20			
	12	36			
	(8)				
	87				
$HgSO_4$	7	33	32	72	25
	10	22	20	74	40
		24	42	69	28
				115	127

Note - Values in parenthesis indicate that a gain in weight was observed.

TABLE ii

The Corrosion of Copper in Contact with Mercury Salts
at 100% Relative Humidity

Mercury Salt (Unweighed)	Weight Change in Copper in 70-Hour Period (in mg.)
$HgSO_4$	(2.0)
	(12.7)
$Hg(NO_3)_2 \cdot H_2O$	(0.2)
	(0.9)

Note - Values in parenthesis indicate that a gain in weight was observed.

TABLE III

The Corrosion of Copper in Contact with Mercury Salts
and H_2S Vapor (Water Vapor Removed by Drying Agent)

Mercury Salt (Unweighed)	Weight Loss of Copper in 70-Hour Period (in mg.)
$HgSO_4$	86
	94
	99
$Hg(NO_3)_2 \cdot H_2O$	81
	83
	80

TABLE IV

The Corrosion of Previously-Amalgamated Copper in an Atmosphere
of H_2S at 100% Relative Humidity

Sample Number	Loss in Weight in a 22-Hour Period (in mg.)
1	3
2	3
3	8
4	6
5	11
6	10
7	15
8	6

TABLE V

The Corrosion of Copper in Contact with Solid Nitrates
in an Atmosphere of H_2S at 100% Relative Humidity

Nitrate (Unweighed)	Weight Loss of Copper in 23-Hour Period (in mg.)
$NaNO_3$	23
$Ca(NO_3)_2$	26
NH_4NO_3	30
$Zn(NO_3)_2$	31
$Bi(NO_3)_3$	51
	80
$Hg(NO_3)_2 \cdot H_2O$	85
$AgNO_3$	334
	399

The very large amount of corrosion observed with $AgNO_3$ in the presence of H_2S and water vapor, as shown in Table V, suggested that experiments should be carried out to determine the importance of H_2S. Table VI summarizes experiments made in the presence and absence of H_2S to test this point. The total amount of corrosion in a 22-hour period was appreciably greater in the presence of H_2S.

The great effectiveness of $AgNO_3$ in increasing the amount of corrosion of copper in the presence of H_2S raised the question as to the chemical reactions that were occurring. In the absence of H_2S and in the presence of a high water vapor concentration, it might be expected that the simple

replacement reaction, $2AgNO_3 + Cu \longrightarrow Cu(NO_3)_2 + 2Ag$, would occur. A series of experiments to test this point are summarized in Table VII. It will be noted that the theoretical weight loss of copper on the basis of this reaction is very close to that actually observed. In 9 of 11 cases the actual loss was slightly greater than the theoretical loss, suggesting that the nitrate ion might also have been effective in oxidizing the copper. It was felt that the nitrate ion might be more effective in oxidizing copper if a better source of hydrogen ions than water was present. To this end the experiments reported in Table VII were repeated in the presence of acetic acid vapor. The source of the vapor was a beaker of concentrated acetic acid placed in the reaction chamber. The results summarized in Table VIII show that under these conditions the theoretical weight loss departs seriously from that expected on the basis of a simple replacement reaction.

If the silver nitrate took part in the reaction in the presence of H_2S in stoichiometric quantity, the likely reaction which might take place is the following: $AgNO_3 + 4Cu + 2H_2S \longrightarrow Ag + NO + 2Cu_2S + 2H_2O$. The results tabulated in Table IX indicate that the weight loss of copper is significantly greater than would be expected on the basis of this type of stoichiometric participation of $AgNO_3$ in the corrosion reaction.

TABLE VI

The Corrosion of Copper in Contact with $AgNO_3$ at 100% Relative
Humidity in the Absence and Presence of H_2S

Weight Loss in 22-hour Period (in mg.)

In Absence of H_2S	In Presence of H_2S
35	109
58	82
	334
	397

TABLE VII

The Corrosion of Copper in Contact with AgNO$_3$ at 100%
Relative Humidity (No H$_2$S Present)

Weight of AgNO$_3$ on Copper Surface	Weight Loss of Copper	Theoretical Weight Loss on Basis of Simple Replacement Reaction	Ratio of Actual Weight Loss to Theoretical Loss
8.1 mg.	1.3 mg.	1.5 mg.	0.87
25	5.5	4.7	1.2
53	11.5	9.8	1.2
67	14	12.5	1.1
80	16	15	1.1
99	21	18	1.1
101	20	20	1.0
125	35	23	1.5
146	33	27	1.2
187	44	35	1.3
278	63	52	1.2

TABLE VIII

The Corrosion of Copper in Contact with AgNO$_3$ at 100%
Relative Humidity in the Presence of Acetic Acid Vapor (No H$_2$S Present)

Weight of AgNO$_3$ on Copper Surface	Weight Loss of Copper	Theoretical Weight Loss on Basis of Simple Replacement Reaction	Ratio of Actual Weight Loss to Theoretical Loss
42 mg.	18 mg.	7.8 mg.	2.3
86	28	16	1.8
121	32	22	1.4
162	48	30	1.6

TABLE IX

The Corrosion of Copper in Contact with $AgNO_3$ at 100% Relative Humidity in the Presence of H_2S

Weight of $AgNO_3$ on Copper Surface	Weight Loss of Copper	Theoretical Weight Loss on Basis of Reaction, $AgNO_3 + 4Cu + 2H_2S \rightarrow Ag + NO + 2Cu_2S + 2H_2O$ *	Ratio of Actual Weight Loss to Theoretical Loss
1.5 mg.	24 mg.	2.2 mg.	11
2.1	31	3.1	9.9
2.5	25	3.7	6.8
3.6	22	5.3	4.2
5.6	25	8.3	3.0
9.1	35	14	2.6
9.5	38	14	2.7
14	53	21	2.6
26	76	39	1.9
46	89	76	1.2
76	103	113	0.9
111	126	166	0.8

* – Note – The reaction which utilizes $AgNO_3$ in an oxidation-reduction system and which would consume the maximum amount of Cu is the following:

$$2AgNO_3 + 18 Cu + 9H_2S \longrightarrow 2Ag + 2NH_3 + 9Cu_2S + 6H_2O$$
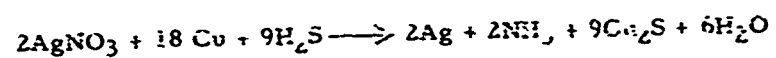
This reaction alone still fails to account for the large amount of copper consumed in the case of small amounts of $AgNO_3$.

The appreciable corrosion caused by nitrate salts in the presence of H_2S raised the question as to whether the function of the H_2S simply was to furnish hydrogen ions so that the nitrate behaved as nitric acid or whether it also participated directly in the reaction. In order to test this point samples of copper were exposed to 0.1 g. of concentrated nitric acid at 100% relative humidity in the presence and absence of H_2S. The results of these experiments are tabulated in Table X. It will be noted that the average weight loss of copper in the presence of H_2S was approximately 7 times the loss in its absence.

TABLE X

The Corrosion of Copper by Concentrated Nitric Acid at 100% Relative Humidity in the Presence and Absence of H_2S in 22-Hour Period

Amount of HNO_3 Used	Weight Loss of Copper	Weight Loss Calcd. on Basis of Reaction, $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 2H_2O$	Weight Loss Calcd. on Basis of Reaction, $3Cu + 2HNO_3 + 2H_2S \rightarrow 3CuS + 2NO + 4H_2O$
		In Absence of H_2S	
100 mg.	17 mg.	38 mg.	
	20	38	
	21	38	
	15	38	
		In Presence of H_2S	
100 mg.	126 mg.		150 mg.
	133		150
	120		150
	112		150
	124		150
	126		150

X-ray Diffraction Studies of the Products Formed in Reactions In-
volving Copper.   A portion of the product was removed from the surface at
the end of an experiment, it was ground in a mortar, and was then packed in
a small capillary tube for diffraction analysis. All X-ray measurements were
made using copper radiation.

(1) Copper, $Hg(NO_3)_2$, H_2S, and moist air. In the presence of an
excess of $Hg(NO_3)_2$, the crystalline products were HgS, CuS, and $Cu(NO_3)_2 \cdot$
$3Cu(OH)_2$.

(2) Copper, $AgNO_3$, H_2S, and moist air. In the presence of an excess
of $AgNO_3$, the crystalline products were Ag, Cu_2S, CuS, and $Cu(NO_3)_2 \cdot$
$3Cu(OH)_2$.   In the presence of a small amount of $AgNO_3$, the crystalline
products were Cu_2S, CuS, and Ag. In all cases there were 10 to 17 lines
which could not be associated with any compounds in the ASTM X-ray Diffrac-
tion Card File.

(3) Copper, $AgNO_3$, acetic acid vapor, moist air. In the presence of
an excess of $AgNO_3$, the crystalline products were Ag and Cu_2O.

(4) Copper, H_2S, moist air. The only crystalline product was Cu_2S.
Nine lines of faint intensity were not identified.

(5) Copper, HNO_3, H_2S, moist air. The crystalline products were
CuS, Cu_2S, and $Cu(NO_3)_2 \cdot 3Cu(OH)_2$.

Experiments with Other Metals. Tables XI, XII, XIII, and XIV
summarize some of the miscellaneous experiments carried out with other
metals and salts in the presence of hydrogen sulfide. It will be noted that the
combination of a nitrate, hydrogen sulfide, and moist air is extremely
corrosive to many metals.

TABLE XI

A Summary of Miscellaneous Experiments on the Corrosion of Various
Metals in the Presence of a Salt, 100% Relative Humidity, and H_2S for
a 22-23 Hour Period

Metal Undergoing Corrosion	Salt Placed on Surface (Unweighed)	Weight Loss of Corroded Metal
Cu	$GaCl_3$	54 mg
		47
		51
		41
		56
		48
Mg	HgF_2	(20)
	$HgCl_2$	(33)
	Hg_2Cl_2	(13)
	$HgBr_2$	12
	HgI_2	17
	$HgSO_4$	1
	$Hg(NO_3)_2 \cdot H_2O$	79
Ti	$AgNO_3$	0
	$AgNO_3$	0.1
	HgF_2	4
	HgF_2	1
Zr	HgF_2	(4)
	HgF_2	(6)
Cd	$AgNO_3$	42
	$AgNO_3$	37
Ni	$Hg(NO_3)_2 \cdot H_2O$	37
	$Hg(NO_3)_2 \cdot H_2O$	45
	$AgNO_3$	72
	$AgNO_3$	80
Sn	$AgNO_3$	42
	$AgNO_3$	50
Fe	$AgNO_3$	150
	$AgNO_3$	154

TABLE XI (cont.)

Metal Undergoing Corrosion	Salt Placed on Surface (Unweighed)	Weight Loss of Corroded Metal
Pb	$HgSO_4$	(12)
	$HgSO_4$	(4)
Stainless Steel 303	HgF_2	15
	HgF_2	24
Zn	$AgNO_3$	49
	$AgNO_3$	51

TABLE XII

The Corrosion of Copper, Nickel, and Iron in Contact with Solid Ag_2S at 100% Relative Humidity in the Absence and Presence of H_2S in a 22-Hour Period

Metal Undergoing Corrosion	Weight Loss in the Absence of H_2S	Weight Loss in the Presence of H_2S
Cu	0.5 mg.	16 mg.
	0.6	22
	0.6	25
	0.5	18
Ni	20	50
	19	52
		41
		37
Fe	8	62
	1.5	86
		105
		106

TABLE XiiI

The Corrosion of Iron by Solid $AgNO_3$ at 100% Relative Humidity in the Absence and Presence of H_2S

Weight of $AgNO_3$ Used	Weight Loss of Iron	Theoretical Weight Loss on Basis of Reaction, $2Fe + AgNO_3 + 2H_2S \longrightarrow Ag + 2FeS + NO + 2H_2O$
In Absence of H_2S		
33 mg.	(0.4)	
55	7	
77	1.5	
118	(2)	
265	1.2	
In Presence of H_2S		
74 mg	30 mg	49 mg
103	43	68
135	76	89
156	45	103
219	59	144
262	99	174

TABLE XIV

The Corrosion of Nickel by Solid $AgNO_3$ at 100% Relative Humidity in
the Presence of H_2S in a 22-Hour Period

Weight of $AgNO_3$ Used	Weight Loss of Nickel	Theoretical Weight Loss on Basis of Reaction, $2Ni + AgNO_3 + 2H_2S \longrightarrow Ag + 2FeS + NO + 2H_2O$
15 mg.	39 mg.	10 mg.
34	45	23
50	68	34
71	57	49
75	61	52
125	72	85
161	76	111
171	78	118
172	73	118
204	82	140
267	90	184
383	102	265

DISCUSSION

The purpose of these experiments was to choose for quantitative study a system showing very rapid deterioration of copper   This purpose was achieved, but quantitative experiments were not initiated because of termination of the contract.

The system consisting of silver nitrate, hydrogen sulfide, and moist air was very corrosive to many metals including copper, nickel, iron, cadmium, tin, and zinc. In the case of copper and nickel, it appeared that the amount of reaction was much greater than would be expected on the basis of the nitrate ion concentration   It is not known, however, whether the silver nitrate was a true catalyst for the reaction of copper with oxygen or hydrogen sulfide or whether simple reaction of hydrogen sulfide with the copper could account for the amount of reaction over and above that called for by a reaction involving nitrate. A decision in this regard must await quantitative experiments.

PART D

"The Very Rapid Oxidation of Aluminum at Room
Temperature When in Contact with Mercuric Iodide"

By

David A. Jackson, Jr., and Henry Leidheiser, Jr.

ABSTRACT

The rate of oxidation of aluminum, contaminated with HgI_2, in moist air occurred linearly with time in the early stages of reaction. The rate of oxidation at $30°C$ increased with relative humidity and was a maximum at 80-100% RH. The majority of the reaction was with oxygen but a constant amount of reaction, 0.066 mg $/cm.^2/$minute, occurred with water vapor over the relative humidity range 36-100%. The total reaction of aluminum at 100% relative humidity was equivalent to 0.9 mg. of aluminum $cm.^2/$minute. The reaction product exhibited no crystalline diffraction pattern when examined with electron or X-ray beams. The product lost a negligible amount of water when heated at $115°C$. but it did lose an average of 34% by weight when heated at $600°C$. Aging of the product without dehydration resulted in the crystallization of the beta-trihydrate. An explanation of the strong dependence of the rate on the relative humidity was given and was based on the supposition that the electrical properties of any film of oxide present on the surface were a function of the relative humidity.

INTRODUCTION

It is well known that mercury has an extremely deleterious effect on aluminum in many environments. For example, the corrosion of aluminum in boiling 2M HCl containing 10^{-4} to 10^{-2}M $HgCl_2$ is increased a 100-fold over that in the absence of mercury (1). Also, the rate of oxidation of aluminum is greatly increased in the presence of mercury as can readily be shown by applying a drop of mercury on an aluminum surface and scratching the surface in order to aid in penetration of the oxide film.

The purpose of the work reported herein was to make a quantitative study of the oxidation of aluminum in the presence of mercury and thereby to determine the more important variables. Preliminary experiments indicated that it was very difficult to obtain reproducible results with metallic mercury, presumably because of the inability to prepare a reproducible surface whose oxide coating was uniformly penetrated by mercury. Preliminary experiments with many mercury salts indicated that HgI_2 was a satisfactory reactant and that uniform attack was obtained over the entire surface when it was spread in a thin layer. Quantitative experiments were then confined to HgI_2

EXPERIMENTAL PROCEDURE

It was determined very early in the research that aluminum in contact with HgI_2 reacted with both oxygen and water vapor when both were present in the atmosphere. The major amount of reaction leading to a pressure change at all humidities took place with oxygen as indicated by the fact that there was a pressure decrease in a closed system containing air when the water vapor concentration was maintained constant. These observations led us to adopt pressure change in a closed system as the measured parameter for following the reaction as a function of time. Since the reaction with oxygen consumes 3/4 mole of oxygen gas for every gram atom of aluminum and the replacement reaction with water evolves 3/2 mole of hydrogen gas for every gram atom of aluminum, a small fraction of the total reaction involving water leads to a significant error in assessing the total amount of reaction from pressure decrease only. Gravimetric measurements were thus carried out in separate experiments in order to determine the relationship between pressure change and the total amount of reaction. As described later, it was found that the rate of the replacement reaction of aluminum with water was constant at relative humidities ranging from 36 to 100% and was not greatly different from the rate of reaction of aluminum with liquid water at the same temperature. All studies were carried out with air.

The reaction apparatus consisted of an insulated, double-walled copper chamber whose interior metal surface was heavily coated with a flat black

paint. The sealed chamber was connected to a mercury capillary manometer at L and to a bellows-type pressure gauge at K. The chamber was maintained at constant temperature by passing water from a constant temperature bath between the double walls of the chamber. Temperature measurements were made by means of a thermometer passing into the chamber at N through an "O" ring seal.

The cylindrical sample was inserted in the plastic holder G which was cemented to the hollow support F through which water at constant temperature continuously circulated. The sample fit very tightly in the holder G so that only the upper circular surface was exposed to HgI_2. The base of the plastic holder G was machined to a thickness of approximately 0.5 mm. so as to interfere as little as possible with the transfer of heat from the specimen to the constant-temperature water circulating through F.

The desired relative humidity was obtained by placing a saturated salt solution in the plastic tray T and allowing the enclosed system to reach equilibrium during a 30-minute period. Both thermal and humidity equilibrium were facilitated by the use of a small fan X which continually stirred the internal atmosphere. At relative humidities less than 100%, Octoil-S was used as a spacer to control the internal volume of the chamber to 1000 cc. At 100% relative humidity, water was used as the spacer.

The HgI_2 was uniformly distributed over the sample surface by passing it through a Nylon sieve E which was agitated by the stainless steel rod C. A

Figure 1. Apparatus used in quantitative studies of oxidation of aluminum in contact with HgI_2.
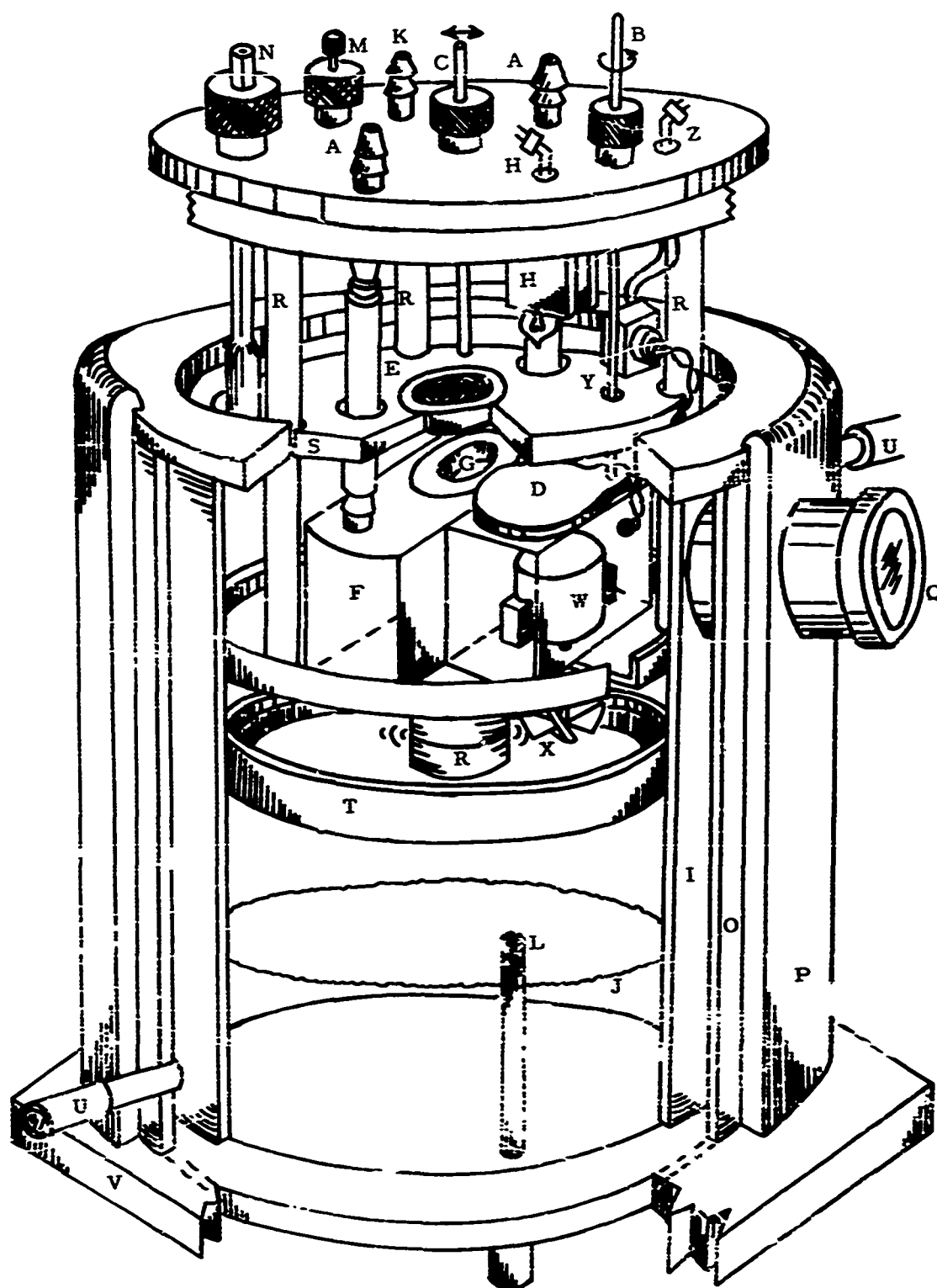
movable shield D prevented specks of the salt from coming into contact with the sample prior to the desired time.

The aluminum samples were prepared from 99 999% pure ingot obtained from Dr. Lee Craig of the Reynolds Metals Company. They were machined in the shape of cylinders, 1.3 cm. in diameter. They were degreased in ether and were heavily etched in ?N HCl immediately prior to insertion into the reaction chamber. The appearance of the sample during the reaction was observed through the observation port Q and illumination was provided by a battery-operated lamp H.

EXPERIMENTAL RESULTS

Rate Measurements

The rate curves, as determined by pressure change uncorrected for water replacement reaction, were all characterized by a linear segment in the early stages as shown by the representative curves in Figs. 2 and 3. At 100% relative humidity and 30°C. there was an induction period which was as long as 40 minutes in some instances. This induction period decreased with decrease in relative humidity at 30°C. and was much less at 40°C. and 100% relative humidity than at 30°C. At low relative humidities the linear rates were not maintained for long periods and the reaction ceased after 100-200 minutes. At high relative humidities the reaction rate decreased as the oxygen in the system approached a low value. A compilation of all the rate measurements is given in Fig. 4 in which the average value of the linear rate is plotted as a function of the relative humidity. The range of all the measurements at any one relative humidity is denoted by the bar.

At high relative humidities (90-100%) the oxide often grew as a continuous, thick, blue-white column. This column grew perpendicularly and had sufficient strength to lift the Nylon sieve from its support. At low relative humidities (20-50%), the oxide consisted of short fibers, somewhat powdery and pure white in color. At intermediate humidities and at high humidities long ribbons of oxide formed. Microscope examination of the point of contact between the aluminum sample and small crystal of HgI_2 indicated that metallic mercury was formed and that it rapidly spread over a large area
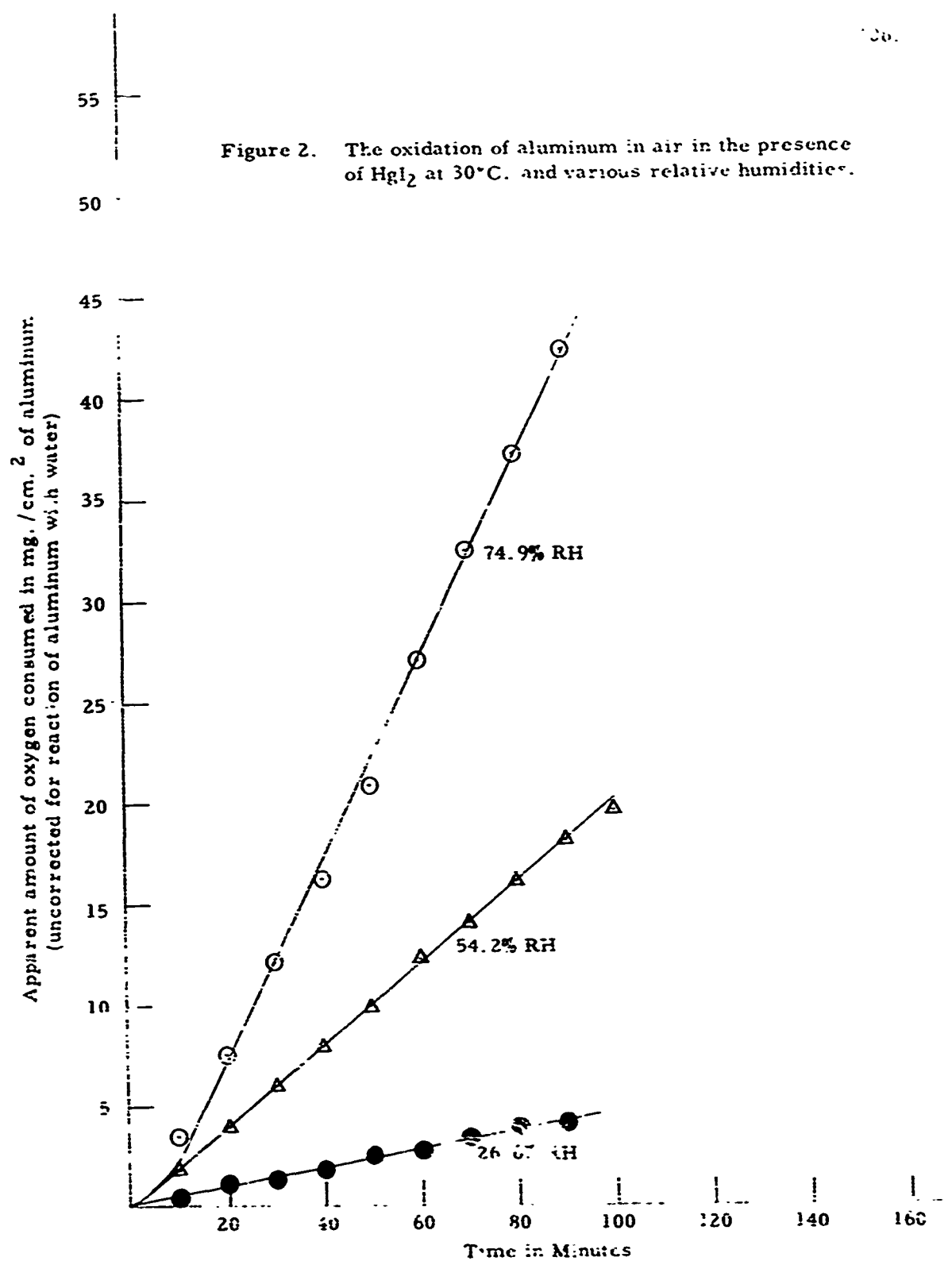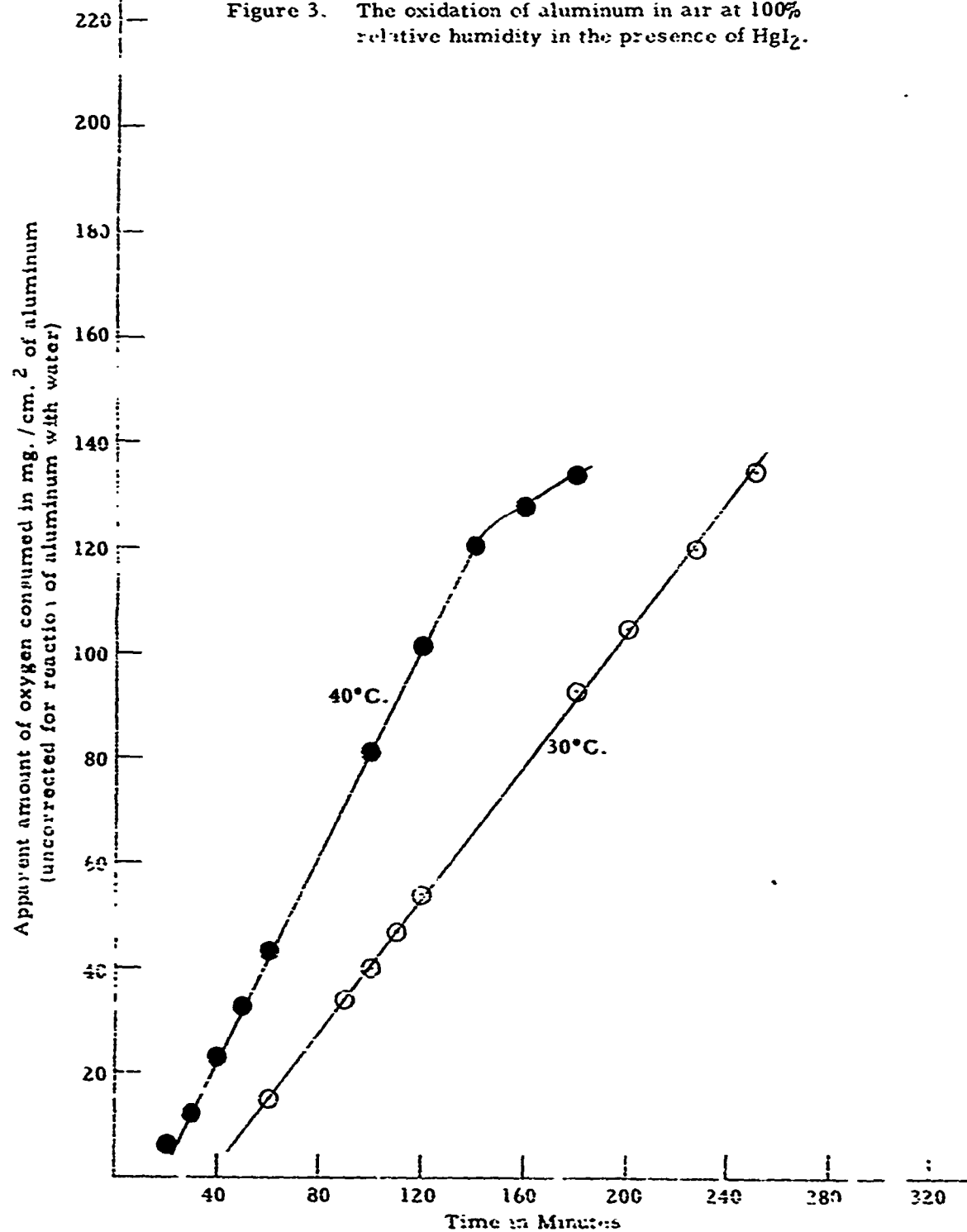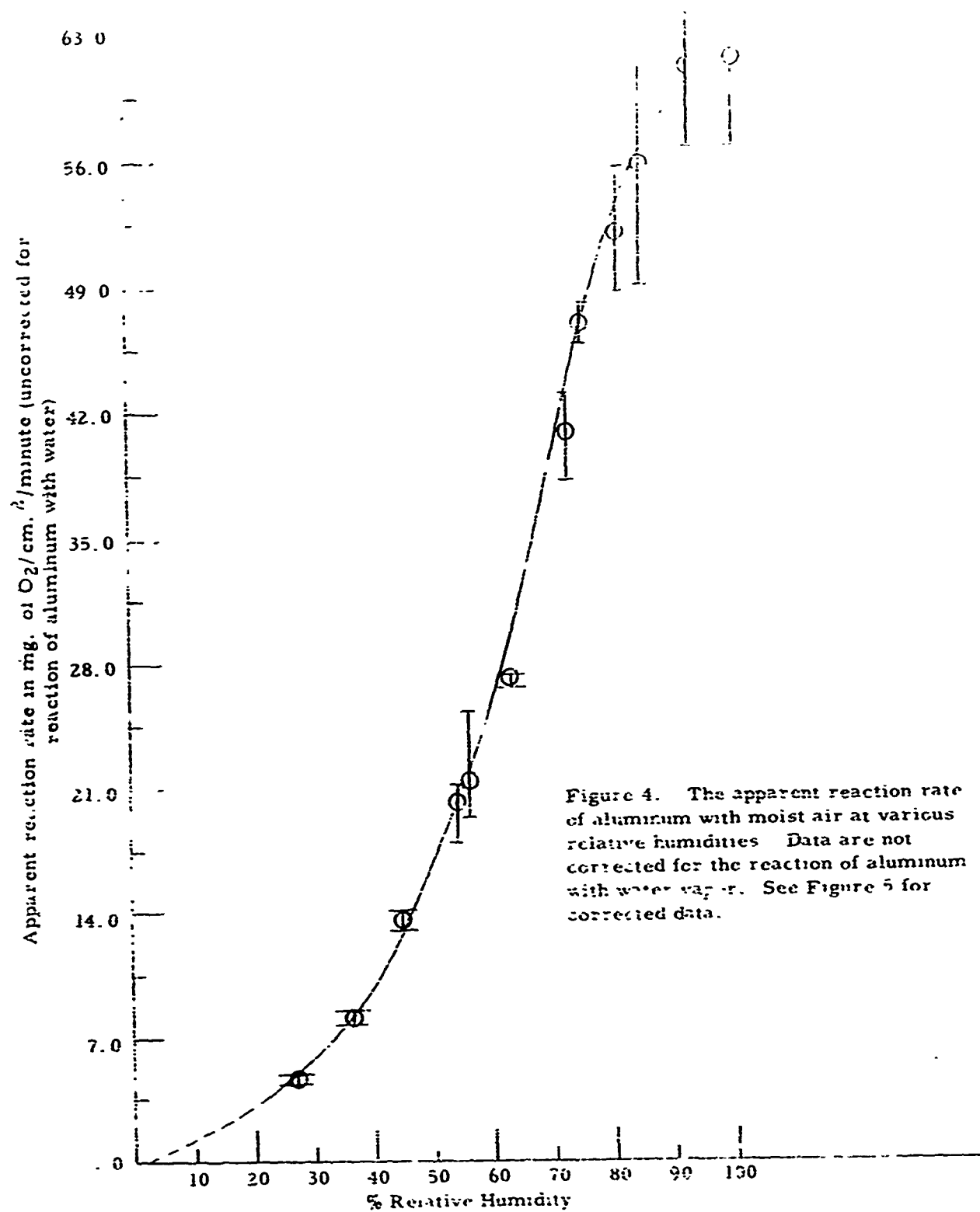
Figure 2.   The oxidation of aluminum in air in the presence of HgI_2 at 30°C. and various relative humidities.

Figure 3. The oxidation of aluminum in air at 100% relative humidity in the presence of HgI_2.

Figure 4. The apparent reaction rate of aluminum with moist air at various relative humidities Data are not corrected for the reaction of aluminum with water vapor. See Figure 5 for corrected data.

from its point of origin. Oxide formed uniformly over the surface in the area covered by the spreading mercury.

As stated previously, it was known that a portion of the total overall reaction involved a replacement reaction of water with aluminum. The method used to determine the fraction of reaction with oxygen and with water vapor was as follows. Three to eight experiments were carried out at each of the following humidities: 36, 58, 73, 81, 85, 93, and 100%. The cylindrical samples of aluminum were rubbed i- $_2$ and were immediately placed in a closed system maintained at the desired humidity. The pressure change during the experiment was measured and the amount of aluminum consumed was determined gravimetrically. The pressure measurements summarized in Fig. 4 were then used to calculate the amount of reaction with oxygen and the amount of the replacement reaction with water. The results of these experiments are summarized in Fig. 5 and Table I. The information tabulated in the right hand column of Table I indicated that the rate of the replacement reaction with water was independent of the water vapor concentration over the range of 36 to 100% relative humidity.
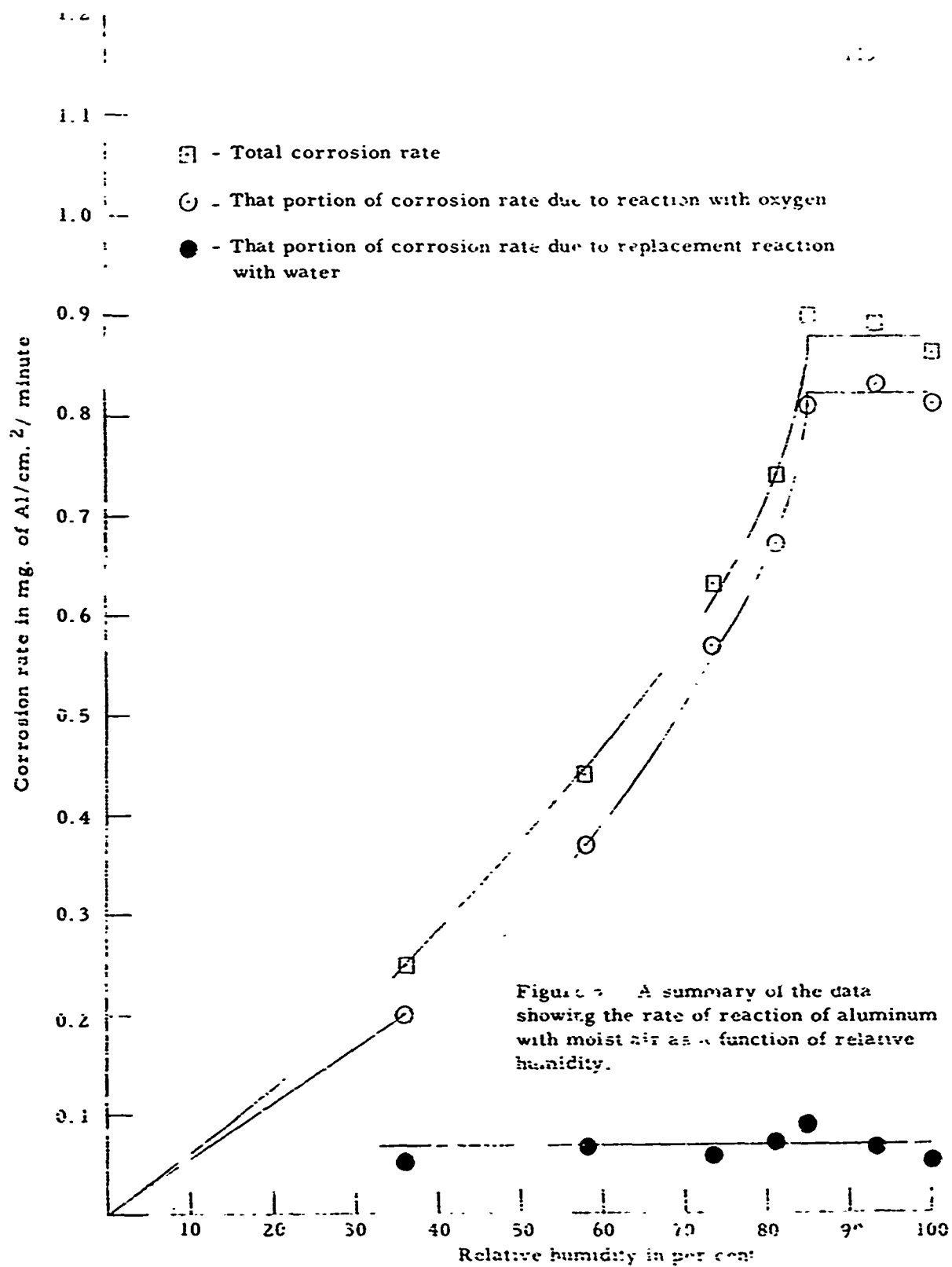
Next, it appeared of interest to determine the rate of corrosion of aluminum in water under essentially the same conditions of amalgamation. Samples of aluminum were coated with HgI_2, the iodide was washed off in a stream of water, and the samples were immersed for 1-24 hours in a 0.001M solution of $HgCl_2$ maintained at 30°. The rate of the reaction in 7 experiments ranged from a low of 0.013 to a high of 0.035 mg./cm.^{2}/min., with an

average rate of 0.020 mg./cm.^{2}/min. Thus the rate of reaction of aluminum

with water vapor (0.066 mg./cm.^{2}/min.) was not greatly different from the

rate of reaction with liquid water.

TABLE I

A summary of the experiments carried out to determine the fraction
of the total reaction accounted for by a replacement reaction between
aluminum and water.

Relative Humidity	Percentage of Total Reaction Involving Water	Calculated Rate of Reaction of Aluminum with Water Assuming a Linear Rate over the Experiment
		mg. of Al/cm.^{2}/minute
100%	18%	0.05
93%	23%	.07
85%	30%	.09
81%	30%	.07
73%	27%	.06
58%	45%	.07
36%	64%	.05
	Average	0.066

Figure 2 — A summary of the data showing the rate of reaction of aluminum with moist air as a function of relative humidity.

Legend:
- ▢ - Total corrosion rate
- ☉ - That portion of corrosion rate due to reaction with oxygen
- ● - That portion of corrosion rate due to replacement reaction with water

Y-axis: Corrosion rate in mg. of Al/cm.^{2}/ minute

X-axis: Relative humidity in per cent

The Oxidation Product

X-ray diffraction analysis of the product immediately after preparation indicated, by the absence of a diffraction pattern, that is was amorphous. This confirmed the observation made previousl, by Straughan (2) on th' product formed when mercury contacted a single crystal of aluminum. Subsequently, Heyn (3) noted that no crystalline pattern was obtained using electron diffraction techniques on the product formed on aluminum in the presence of mercury under room conditions. Lawless (4) confirmed that the product formed in the presence of HgI_2 at 100% relative humidity yields no crystalline diffraction pattern using electron diffraction techniques.

Exposure of the oxide to 100% relative humidity at room temperature for 10-21 days resulted in the crystallization of beta-$Al_2O_3 \cdot 3H_2O$. The rate of crystallization of the trihydrate appeared to be greater for the product formed at 40°C. and 100% relative humidity than at 30°C. Simultaneously with the crystallization, the sample decreased greatly in volume and it changed from its bluish-white translucent appearance to an opaque white color.

Dehydration of the product at 600°C. for 3 hours resulted in a product which yielded no diffraction pattern. Rehydration of this dehydrated product by exposure to 100% relative humidity for 10 days resulted in the crystallization of the beta-trihydrate. Dehydration of the crystalline hydrate formed by hydration of the dehydrated, initially-formed, amorphous oxide yielded anhydrous eta-Al_2O_3. The pattern obtained in this case was diffuse

Negligible weight losses were obtained when the oxidation product was heated at 115°C. for 1-10 hours. An estimate of the amount of water in the product was obtained by determining the weight loss when the sample was heated at 600°C. for 3 hours. Analyses were performed on products formed at 81 and 100% relative humidity at 30°C. and at 100% relative humidity at 40°C. The weight loss in eight samples ranged from a low of 31 0% to a high of 38.9% with an average loss of 33.7%. The difficulty in making accurate measurements of this type is a result of the fact that droplets of mercury and HgI_2 are occasionally trapped in the oxide during growth. This weight loss suggests that the approximate composition of the product is $Al_2O_3 \cdot 3H_2O$, in which the theoretical water content is 34.6% by weight.

DISCUSSION

These experiments furnish additional convincing evidence for the highly reactive nature of aluminum when its oxide film no longer offers protection. The rate of oxidation in air at high relative humidity and 30°C., for example, was equivalent to the consumption of 0.9 mg. of aluminum/cm.^{2}/ minute. The non-protective nature of the reaction product was emphasized by the fact that the rate of reaction was linear with time as shown by experiments of the type reported in Fig. 2. Such rates are often obtained with systems in which the reaction product develops faults such as cracks or pores.

Attempts to furnish a quantitative explanation for the oxidation behavior are severely limited by the inability to make measurements on or observation of the aluminum surface during reaction. The dynamic nature of the surface and the presence of the voluminous reaction product precluded simultaneously rate measurements, and meaningful electrical measurements, for example. It has been necessary, therefore, to attempt an explanation on the basis of measurements on samples of other types and on the basis of the electron microscope observation of Heyn (3).

The optical microscope studies indicated that the HgI$_2$ rapidly reacts with aluminum and the resulting free mercury spreads over the surface from its point of origin.

It is conjectured that the oxide film which forms on the mercury-contaminated aluminum surface is similar to that which is formed during

anodic treatment (5) in which pores penetrate the oxide normal to the metal surface. These pores have been determined to be 100-300 A. in diameter by electron microscope observations (6). It is further conjectured that the major fraction of the total oxidation of aluminum under the conditions used in these experiments is electrochemical in nature with the simple empirical anodic reaction being represented by $Al - 3e^- = Al^{+++}$ and the simple empirical cathodic reaction by $O_2 + 4e^- = 2O^=$. The rate under a certain range of experimental conditions might then be determined by the electrical properties of the oxide. Jason and Wood (5), and more recently Stover (7), have found that the impedance of anodically-formed oxide films is a function of the relative humidity of the atmosphere surrounding the sample. Stover found, for example, that the impedance of an aluminum sample anodized in 50% sulfuric acid at 90°F. and 12 amp./sq. ft. for 25 minutes was approximately 10^6 ohms at 0 relative humidity, 10^5 ohms at 40% relative humidity, 10^4 ohms at 60% relative humidity, and approximately 2×10^3 ohms at 100% relative humidity.

Jason and Wood found that the equivalent parallel resistance decreased from the order of 10^7 ohms at 0% relative humidity to approximately 3×10^3 ohms at 100% relative humidity for films formed by anodization in chromic acid, oxalic acid, and sulfuric acid. The equivalent parallel capacitance increased from $5 \times 10^2 - 2 \times 10^3$ microfarads at 0% relative humidity to 3×10^5 microfarads at 100% relative humidity for samples anodized in the same three electrolytes.

If the properties of the films present on the surface in this study and
the films studied by Jason and Wood are similar, then it may be said that
the electrical properties are strongly a function of the relative humidity.
Further, if the reaction is indeed electrochemical in nature, it is to be ex-
pected that the rate would be intimately related to the electrical properties
of the film.

It is proposed that the passage of aluminum ions through the film
occurs largely at pores whose diameter is of the order of 100 A. The electron
micrograph of Heyn (3) clearly shows that the oxidation product is needle-
like in nature. Transport of aluminum ions through the pores apparently
occurs readily and reaction with oxygen and water molecules apparently
occurs within the pore or at the top surface. Transport of aluminum ions
through the film necessitates the transport also of electrons. Their ready
transport perhaps occurs at places where mercury penetrates through the
film, but they may also move through the film at other locations.

The location of the pores in the film probably continually change as
the aluminum at the base of the pore is consumed. Transport of aluminum
atoms at the base of the pore may be facilitated by the presence of mercury
and by the highly exothermic nature of the oxidation process.

The role of water in the reaction is a very complex one. It is apparent
that the influence of water on the overall rate of the oxidation of aluminum is
more than simply an effect on the electrical properties of the film since

water is an intimate component of the reaction product. Very little of the
incorporated water was lost on heating at 115°C. and the composition of the
product as determined by dehydration at 600°C. was equivalent to $Al_2O_3 \cdot 3H_2O$
Storage at 100% relative humidity also led to crystallization of the trihydrate.
Water also was involved in a direct chemical reaction over the entire range
of relative humidity in an amount equivalent to 0.066 mg. of aluminum/cm.^{2}/
minute.

ACKNOWLEDGMENT

BIBLIOGRAPHY

(1)   W. Roger Buck, III, and H. Leidheiser, Jr., Corrosion 14, 308t
        (1958).

(2)   V. E. Straughan, Virginia Journal of Science 3, 311 (1952).

(3)   A. N. J. Heyn, J. Electrochem. Soc. 108, 482 (1961).

(4)   K. Lawless, private communication

(5)   A. C. Jason and J. L. Wood, Proc. Phys. Soc. 68B, 1105 (1955).

(6)   F. Keller, M. S. Hunter, and D. L. Robinson, J. Electrochem. Soc.
        100, 411 (1953).

(7)   C. M. Stver, "New Aluminum Oxide Humidity Element," Sandia
        Corporation, Technical Memorandum, March, 1962.

PART E

"An Ultrastructure Study of the Corrosion Product Formed
during the Catastrophic Corrosion of Aluminum in the
Presence of Mercury and an Hypothesis for Explaining the
Structure Observed"

By

Anton N. J. Heyn

ABSTRACT

An electron microscope study was made of the product formed when mercury and mercury alloys were contacted with aluminum in air at room temperature. The structure of the product consisted of uniform, elongated micellar strands, approximately 100 A. in width and 2000 A. or more in length. An hypothesis of alternating active sites was proposed. Electron diffraction studies gave no evidence that the product was crystalline.

It has long been known[1] that upon exposure of aluminum to mercury a remarkably destructive type of corrosion occurs in which most fantastically shaped fibrous filaments, bands and sheets of aluminum hydroxide[1] or hydrated aluminum oxide seem to grow rapidly from the metal surface. This particular type of corrosion is most detrimental and extremely difficult to stop, once started.

An ultrastructure study of this phenomenon with the electron microscope has been carried out by the author, the results of which are briefly reported herein.

From the electron micrographs, which are reproduced at a magnification of 23,560 times, it is seen that in all cases the corrosion product has a typical ultrastructure which at first sight looks like a polycrystalline configuration. The composite structure consists of sub-microscopic, uniform, elongated micellar strands or needles, which are bundled together over larger ranges in almost parallel orientation. These needles very often appear to be flattened and have an almost uniform width of about 100 A. Indications of a helical or coiling appearance is often observed. The length of the needles or strands is very difficult to determine. but is generally at least twenty times the diameter, but very often much longer. Transverse ruptures are often seen across the needles. The impression is obtained that longer strands

(1)   H. Röhrig Aluminum Zerstörung durch Quecksilber und ihre
       Bekämpfung. Korrosion und Metallschutz 3, 1 (1927).

are broken at irregular places into shorter pieces to form the needles.

Sometimes consistent large patches of very high electron absorption (appearing white on electron micrograph #4) are observed, which are probably micro droplets of mercury carried along and captivated by the growing fibers. In the vicinity of these drops much finer fibers are often seen.

When other metals have been added to the mercury, such as lead and thallium, the shape and size of the strands is somewhat different. They are more compressed in length and more irregular in appearance and orientation (electron micrograph #5).

A few electron diffraction observations were made for determining whether or not these strands have crystalline configuration. At first sight they usually give the impression of having micro crystalline nature. No clear electron diffraction was obtained, so that the conclusion must be made that the particles are probably amorphous.

The explanation of the remarkable structure observed has to be based on the physical-chemical process underlying its formation. The findings on the structure inversely may point to the nature of this process. On the basis of the above observation the following explanation is presented by the author.

The essential features of the ultrastructure observed is the presence of elongated micro fibrils of rather constant diameter, grown from the surface and packed in parallel orientation. Similar formations have been observed in the case of so-called ' metal whiskers," which are also elongated structures grown from a metal surface along one direction. A difference is

that in the present case the fibers have apparently no crystalline configura-
tion, so that crystalline forces probab', do not play a part in their growth.
The author, therefore, suggests the use of the term "amorphous whiskers"
for the present structures.

It has long been assumed[1] that the aluminum hydroxide is formed in
this corrosion process under dissolving of the aluminum in the fluid mercury
layer covering its surface to form an aluminum-mercury alloy and under
subsequent oxidation of this alloy in contact with moist air.

Assuming that this is correct, the following hypothesis for the details
of this process can be presented on the basis of the ultrastructure observed.
The oxidation of the aluminum alloy will take place in anodic regions which
alternate with cathodic regions on the surface. After the first layer of oxide
has covered the anodic sites, further oxidation will result in the growth of
parallel fibers of infinite lengths in vertical direction, separated at the foot
by the cathodic regions. As a result of growth pressure and maybe also
shifting of the anodic regions over the surface, coiling, transverse rupture
and shifting of the fibers may occur. This would fully explain the features
observed. If this hypothesis is correct, the cross section of the fibers
would essentially correspond to the area of the anodic domains and the cross
section of the composite fibers would be a true representation of this distri-
bution of anodic and cathodic regions on the surface. From the cross sections
of the fibers it could be concluded then that the cross section of the anodic
sites would be about 100 A. and from the packing of the fibers it could be

concluded that the packing is probably not much more than twice this value.

This hypothesis of alternating sites would nicely explain the main point, why a discontinuous arrangement of whiskers is formed rather than a continuous layer of oxide.
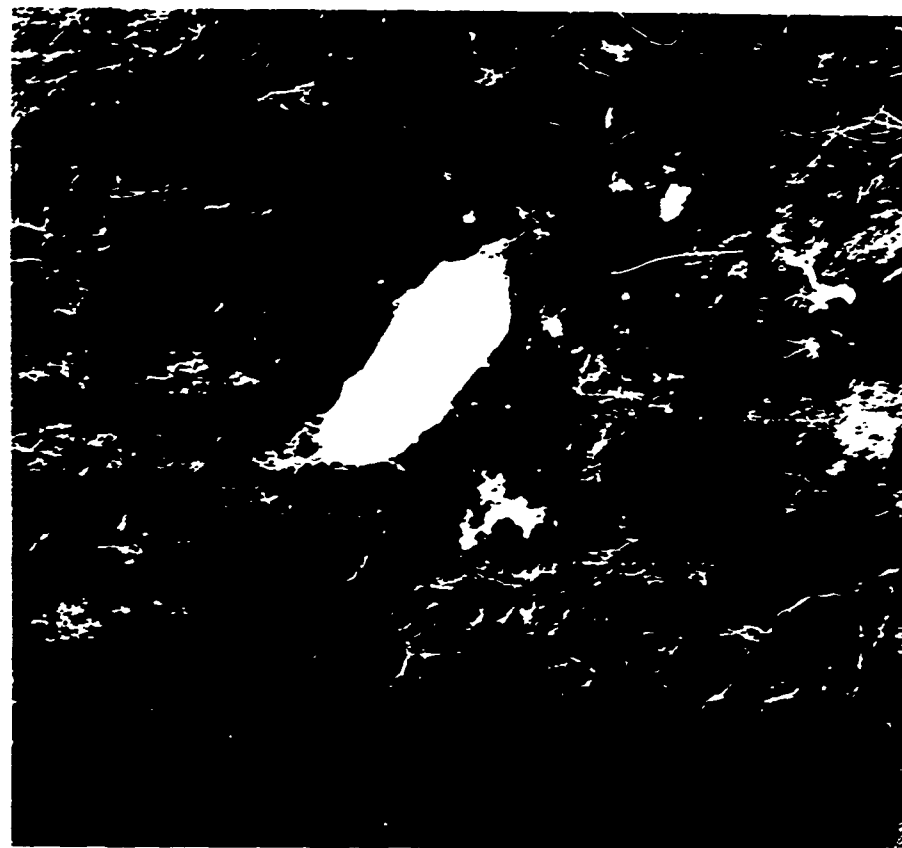
No. 1.   Catastrophic corrosion of aluminum by pure mercury.
         Fibrils almost in original arrangement. The direction
         of growth is perpendicular to the metal surface and
         along the meridian of the photograph. Magnification
         23,560 X.

No. 2.   Catastrophic corrosion of aluminum by pure mercury.
         Fibrils spread out from original arrangement to show
         their shape better. Magnification 23,560 X.

No. 3.   Catastrophic corrosion of aluminum by pure mercury.
         Fibrils spread out from original arrangement to show
         their shape better. Magnificatio. 23,560 X.

No. 4.   Catastrophic corrosion of aluminum by pure mercury
         In center of picture a droplet of mercury surrounded by
         needles of finer structure. Magnification 23,560 X.

No. 5.   Catastrophic corrosion of aluminum by mercury to
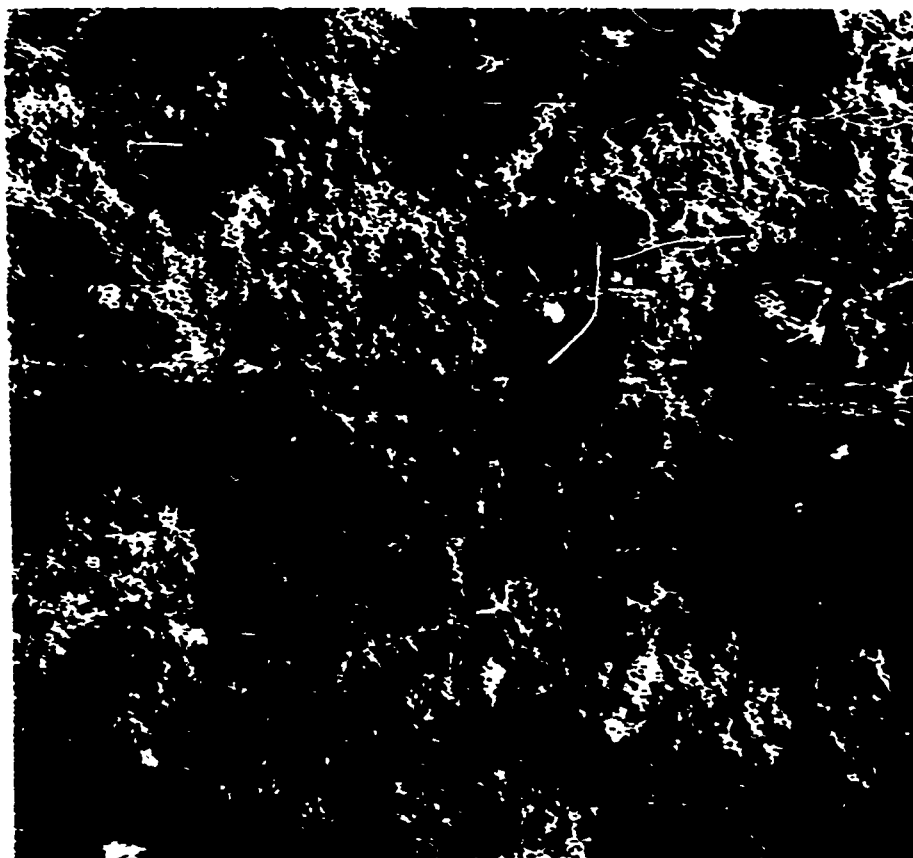   which 20% thallium has been added. Magnification
         23,560 X.

ACKNOWLEDGMENTS